Kinetics of carbon monoxide oxidation over supported platinum catalysts : the role of steam in the presence of ceria

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Kinetics of Carbon Monoxide Oxidation over Supported Platinum Catalysts

The Role of Steam in the Presence of Ceria

Maarten Campman
Kinetics of Carbon Monoxide Oxidation over Supported Platinum Catalysts

The Role of Steam in the Presence of Ceria

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de Rector Magnificus, prof.dr. J.H. van Lint, voor een commissie aangewezen door het College van Dekanen in het openbaar te verdedigen op 3 juni 1996 om 1600 uur.

doors

Maarten Antoon Jan Campman

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SUMMARY

Removal of harmful components from automotive exhaust is commonly achieved by application of a so-called three way catalytic converter, located in the exhaust pipe of a car. These converters consist of a monolith reactor with several thousands of parallel channels coated with a washcoat layer. The washcoat consists of platinum, rhodium and/or palladium dispersed on an alumina support, which often contains a considerable amount of ceria and small amounts of additives.

The catalytic oxidation of CO by oxygen on washcoat catalysts was studied in a laboratory fixed-bed reactor, and both a commercial Pt/Rh/\(\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3\) catalyst and model catalysts were used. Emphasis was put on the intrinsic kinetics of the reaction both in the absence and in the presence of steam. Therefore, by application of the appropriate design criteria, the catalyst bed dimensions were optimised as to minimise the effect of heat and mass transport and transfer on the measured kinetics. The effect of radial temperature gradients was minimised by diluting the catalyst with inert, non-porous \(\alpha\text{-Al}_2\text{O}_3\) pellets. The experiments were performed under process conditions relevant to the practical use of automotive catalysts below the light-off temperature. The reactor was operated differentially and only intrinsic CO$_2$ production rates were accepted for the kinetic analysis.

In the kinetic investigation using a Pt/\(\gamma\text{-Al}_2\text{O}_3\) catalyst the temperature was varied from 463 to 503 K, the CO partial pressure from 0.22 to 8.3 kPa, the oxygen partial pressure from 0.37 to 8.3 kPa, the steam partial pressure from 0 to 10 kPa and the CO$_2$ partial pressure from 0 to 10 kPa, at a constant total pressure of 110 kPa. The CO/O$_2$ ratio in the feed was varied from 0.1 to 3, and the amount of catalyst from 2 \(\times\) 10$^{-4}$ to 6 \(\times\) 10$^{-4}$ kg.

The CO$_2$ production rate was proportional to the oxygen partial pressure and inversely proportional to the CO partial pressure. Adding up to 10 vol% of CO$_2$ to the feed did not significantly affect the CO$_2$ production rate. Elementary step modelling of the kinetics in the absence of steam showed that the kinetics could be most adequately described by a rate
SUMMARY

equation based on the assumption that the CO₂ production rate is limited by molecular chemisorption of oxygen while chemisorbed CO is the most abundant reaction intermediate. Molecular oxygen chemisorption is followed by potentially fast dissociation and reaction with CO. No discrimination could be made between a Langmuir-Hinshelwood surface reaction of chemisorbed CO molecules with O adatoms or an Eley-Rideal reaction of O adatoms with CO from the gas phase, since in the reaction path the CO₂ production step is kinetically insignificant under the process conditions considered. Assessment of the Arrhenius parameters showed that this reaction path led to physically meaningful estimates, in contrast to reaction paths based on dissociative chemisorption of oxygen in one step.

Investigating the effect of the steam partial pressure on the CO₂ production rate revealed that rate enhancement by a factor of approximately two occurred over the whole range of steam partial pressures. This virtually zeroth order dependence on the steam partial pressure of the CO₂ production rate could not be modelled using the elementary reaction step approach. Over the range of process conditions applied, however, the kinetics could be described with statistical significance using the rate equation deduced for the reaction in the absence of steam.

In the investigation of the kinetics of CO oxidation on the commercial catalyst the role of ceria and the effect of steam on the production rate of CO₂ were emphasised. From a comparative study of the commercial catalyst and model catalysts it was found that the behaviour of the commercial catalyst was dominated by the presence of platinum. Ceria was found to enhance the CO₂ production rate by establishing a larger fraction exposed noble metal atoms and by catalyst bifunctionality. Steady state isotopic transient experiments showed that ceria lattice oxygen does not play an important role in CO₂ production over the range of process conditions considered.

The kinetics could be qualitatively described by two parallel reaction paths. The monofunctional path describes CO₂ production via the reaction path proposed for CO oxidation on Pt/γ-Al₂O₃, while the bifunctional path describes the reaction of CO chemisorbed on noble metal sites with oxygen species on the ceria surface. The contribution of each reaction path to the production of CO₂ is a function of the process conditions. This explains the observation that the rate enhancement by ceria increased at larger CO/O₂ ratios in the feed: the reaction on noble metal sites is inhibited by CO which increases the relative importance of the bifunctional reaction path.

The presence of steam was found to enhance the CO₂ production rate on the commercial Pt/Rh/CeO₂/γ-Al₂O₃ catalyst while no significant water-gas shift activity was observed under the process conditions. In order to explain this behaviour a reaction path was proposed parallel to those describing the kinetics in the absence of steam. The effect of steam is described by interaction on the ceria surface between molecularly chemisorbed oxygen and hydroxyl species, creating a larger steady-state concentration of oxygen atoms on the ceria surface. This reaction path was validated by steady state isotopic transient experiments. It was observed that the majority of CO₂ produced contained an oxygen atom originating from steam,
rather than from $O_2$. Steam containing an oxygen atom from $O_2$ was produced at a rate equal to that of $CO_2$ containing an oxygen atom from steam. This could be explained by the reaction path mentioned, assuming adsorption equilibrium of water on ceria.

In practice, the composition of exhaust gas entering an automotive converter oscillates in time around the stoichiometric composition, as a result of the feedback gas composition controller applied. This forced concentration cycling may alter the performance of the catalyst with respect to steady-state operation. Moreover, concentration cycling experiments are an aid in kinetic parameter estimation and kinetic model discrimination.

Studying the effect of forced concentration cycling on the time-averaged $CO$ conversion requires a reproducible concentration waveform, independent of the cycling frequency. In kinetic modelling studies the shape of the concentration cycles as such is irrelevant as long as both the reactor inlet and outlet compositions can be measured with sufficient time resolution. Additionally, it is essential that the concentrations measured at the reactor outlet are not biased by physical transport phenomena in the reactor. Square wave concentration cycling was accomplished by alternatingly feeding two gas streams with different reactant concentrations. The specific requirements were met by using a novel reactor section lay-out characterised by the absence of significant mixing of sequential gas 'packages' in combination with a modified mass spectrometer allowing chemical gas analysis at a rate of 70 Hz.

Experiments using an inert tracer showed that forced concentration cycling experiments could be performed at frequencies up to 5 Hz. An experiment in which the $CO$ and $O_2$ concentrations were cycled in counterphase showed that under specific conditions the time-averaged $CO$ conversion increased by a factor of five relative to steady-state operation. Moreover, this experiment showed that application of forced concentration cycling in kinetic modelling is promising.

The intricate relationship between chemistry and physics in automotive catalytic converters presents the opportunity to optimise the catalyst performance using kinetic mechanisms obtained from experimental data acquired under well-defined conditions. The behaviour of an industrial automotive catalyst was simulated under process conditions relevant to the warm-up period of the converter. The rate equation deduced for $CO$ oxidation on Pt/$\gamma$-Al$_2$O$_3$ was incorporated in a one dimensional heterogeneous model of a monolith reactor. Even at low temperatures non-isothermal effects should be taken into account, since considerable axial temperature gradients develop in the reactor. Furthermore, heat and mass transfer limitations between the washcoat and gas phase should be considered since they significantly affect the simulation results.

Two examples of catalyst performance optimisation by reactor simulations were presented. Application of Pt loading according to a degressive profile through the reactor may improve the $CO$ oxidation activity, enabling a more efficient use of noble metals. Furthermore, air addition to the exhaust stream upstream of the converter may increase the $CO$ conversion after a cold start, provided the air mass flow rate is carefully adjusted to the exhaust gas temperature.
SAMENVATTING

Schadelijke componenten uit autouitlaatgas worden gewoonlijk verwijderd met een zogeheten driewegkatalysator, die zich in de uitlaatpijp van een auto bevindt. Een driewegkatalysator bestaat uit een monolietreactor met duizenden parallelle kanalen bedekt met een washcoat. De washcoat bestaat uit platina, rhodium en/of palladium gedispergeerd op een alumina drager, die vaak een aanzienlijke hoeveelheid ceria en kleine hoeveelheden additieven bevat.

De katalytische oxydatie met zuurstof op washcoat-katalysatoren werd bestudeerd in een laboratorium vast-bedreactor, en zowel een commerciële Pt/Rh/CeO₂/γ-Al₂O₃ katalysator als modelkatalysatoren werden gebruikt. De nadruk werd gelegd op de intrinsieke kinetiek van de reactie, zowel in aanwezigheid als in afwezigheid van stoom. Hiertoe werden de afmetingen van de reactor geoptimaliseerd, gebruikmakend van de juiste ontwerpcriteria, om het effect van stof- en warmtetransport en -overdracht op de gemeten kinetiek te minimaliseren. Het effect van radiale temperatuurgradiënten werd geminimaliseerd door de katalysator te verdunnen met inerte, niet-poreuze α-Al₂O₃ korrels. De experimenten werden uitgevoerd onder procescondities die relevant zijn voor het praktisch gebruik van autokatalysatoren beneden de ontstekingstemperatuur. De reactor werd differentieel bedreven en alleen intrinsieke CO₂ produktiesnelheden werden geaccepteerd voor de kinetische analyse.

In het kinetisch onderzoek met een Pt/γ-Al₂O₃ katalysator werd de temperatuur gevarieerd van 463 tot 503 K, de CO partiaalspanning van 0.22 tot 8.3 kPa, de zuurstofpartiaalspanning van 0.37 tot 8.3 kPa, de stoompartiaalspanning van 0 tot 10 kPa en de CO₂ partiaalspanning van 0 tot 10 kPa, bij een constante totale druk van 110 kPa. De CO/O₂ verhouding in de voeding werd gevarieerd van 0.1 tot 3, en de hoeveelheid katalysator van 2 × 10⁻⁴ tot 6 × 10⁻⁴ kg.
De CO₂ produktiesnelheid was evenredig met de zuurstoffpartiaalspanning en omgekeerd evenredig met de CO partiaalspanning. De toevoeging van CO₂ aan de voeding tot 10 vol% beïnvloedde de CO₂ produktiesnelheid niet in belangrijke mate. Modellering van de kinetiek in afwezigheid van stoom aan de hand van elementaire reaktiestappen liet zien dat de kinetiek het meest adequaat kon worden beschreven door een snelheidsvergelijking gebaseerd op de onderstelling dat de CO₂ produktiesnelheid wordt gelimiteerd door moleculaire chemisorptie van zuurstof, terwijl het katalysatoroppervlak nagenoeg volledig bedekt is met gechemisorbeerd CO. Moleculaire chemisorptie van zuurstof wordt gevolgd door potentieel snelle dissociatie en reactie met CO. Er kon geen onderscheid gemaakt worden tussen een Langmuir-Hinshelwood oppervlakreactie van gechemisorbeerde CO moleculen met zuurstofadatomen en een Eley-Ridealreactie van zuurstofadatomen met CO uit de gasfase omdat de CO₂ produktiestap in het reactiepad kinetisch niet-significant is onder de beschouwde procescondities. Beoordeling van de Arrheniusparameters toonde dat dit reactiepad tot fysisch zinvolle schattingen leidde, in tegenstelling tot reactiepaden gebaseerd op dissociatieve chemisorptie van zuurstof in één stap.

Onderzoek naar het effect van de stoompartiaalspanning op de CO₂ produktiesnelheid liet zien dat snelheidsverhoging met ongeveer een factor twee optrad over het gehele domein van stoompartiaalspanningen. Deze vrijwel nulde-orde afhankelijkheid van de CO₂ produktiesnelheid van de stoompartiaalspanning kon niet gmodelleerd worden uitgaande van de elementaire-stapaanpak. Over het gebied van procescondities kon de kinetiek echter statistisch significant beschreven worden met de snelheidsvergelijking die afgeleid voor de reactie in afwezigheid van stoom.

In het onderzoek van de kinetiek van CO oxydatie op de commerciële katalysator lag de nadruk op de rol van ceria en het effect van stoom op de produktiesnelheid van CO₂. Uit een vergelijkende studie van de commerciële katalysator en modelkatalysatoren bleek dat het gedrag van de commerciële katalysator werd gedomineerd door de aanwezigheid van platina. Ceria vergrootte de CO₂ produktiesnelheid door het tot stand brengen van een grotere fractie van blootgestelde metaalatomen en door bifunctionaliteit van de katalysator. Stationaire-toestandsexperimenten met isotooptransiënten lieten zien dat roosterzuurstof van ceria onder de beschouwde procescondities geen belangrijke rol speelt in de produktie van CO₂.

De kinetiek kon kwalitatief beschreven worden door twee parallelle reactiepaden. Het monofunctionele pad beschrijft CO₂ produktie via het reactiepad dat werd voorgesteld voor CO oxydatie op de Pt/γ-Al₂O₃ katalysator, terwijl het bifunctionele pad de reactie beschrijft van op edelmetaalplaatsen gechemisorbeerd CO met zuurstofspecies op het ceriaoppervlak. De bijdrage van ieder reactiepad aan de produktie van CO₂ is een functie van de procescondities. Dit verklaart de observatie dat de snelheidsvergroting door ceria toeneemt bij toenemende CO/O₂ verhoudingen in de voeding: de reactie op edelmetaalplaatsen wordt geënhibeerd door CO waardoor het relatieve belang van het bifunctionele pad toeneemt.

De aanwezigheid van stoom bleek de CO₂ produktiesnelheid op de commerciële Pt/Rh/CeO₂/γ-Al₂O₃ katalysator te vergroten, terwijl onder de procescondities geen belangrijke
activiteit van de water-gasshiftreactie werd waargenomen. Om dit gedrag te verklaren is een reactiepad voorgesteld parallel aan degenen die de kinetiek beschrijven in afwezigheid van stoom. Het effect van stoom wordt beschreven door interactie op het ceriaoppervlak tussen moleculair gechemisorbeerd zuurstof en hydroxylspecies, waardoor een grotere stationaire-toestandconcentratie van zuurstofatomen op het ceriaoppervlak wordt gecreëerd. Dit reactiepad werd gevalideerd door middel van transiente isotoopexperimenten. Het bleek dat het grootste deel van geproduceerd CO₂ een zuurstofatoom afkomstig van water bevatte, in plaats van een zuurstofatoom afkomstig van O₂. Stoom dat een zuurstofatoom afkomstig van O₂ bevatte werd geproduceerd met een snelheid gelijk aan die van CO₂ dat een zuurstofatoom van stoom bevatte. Dit kon verklaard worden met het genoemde reactiepad, onder onderstelling van adsorptie-evenwicht voor water op ceria.

In de praktijk oscilleren de samenstelling van uitlaatgas dat een autoutlaatgaskatalysator binnenaat rond de stoechiometrische, als gevolg van de toegepaste feed-back regelaar voor de gassamenstelling. Dit gedwongen oscilleren van de concentraties kan de prestatie van de katalysator in vergelijking met de stationaire toestand veranderen. Bovendien zijn experimenten met gedwongen oscillatie van concentraties een hulpmiddel voor schatting van kinetische parameters en van kinetisch-modeldiscriminatie.

Het bestuderen van het effect van gedwongen oscillatie van concentraties op de tijdgemiddelde CO conversie vereist reproduceerbare concentratiegolven, onafhankelijk van de frequentie van de oscillatie. In kinetische modellerstudies is de vorm van de concentratie-oscillatie op zich niet relevant zolang zowel de reactoringangs- als -uitgangssamenstelling met een voldoende tijdresolutie gemeten kunnen worden. Daarbij is het essentieel dat de concentraties gemeten aan de reactoruitgang niet worden beïnvloed door fysische transportverschijnselen in de reactor. Concentraties in de reactor konden in de tijd blokgolfsgewijs worden gevarieerd door twee gasstromen met verschillende reactantconcentraties alterneren te voeden. Aan de specifieke eisen werd voldaan door een nieuwe indeling van de reactorsectie, gekenmerkt door de afwezigheid van significante menging van opeenvolgende 'gaspakketjes', in combinatie met een aangepaste massaspectrometer die chemische gasanalyse toelaat met een frequentie van 70 Hz.

Experimenten met een inerte tracer lieten zien dat experimenten met geforceerde oscillatie van concentraties konden worden uitgevoerd met frequenties tot 5 Hz. Uit een experiment waarin de concentraties van CO en O₂ in tegenaan oscilleerden werd gevonden dat onder bepaalde condities de CO conversie in verhouding tot de stationaire toestand met een factor vijf toenam. Bovendien liet dit experiment zien dat toepassing van dit type experimenten in modellering van kinetiek veelbelovend is.

Het ingewikkelde verband tussen chemie en fysica in autoutlaatgaskatalysatoren biedt de mogelijkheid tot het optimaliseren van de prestatie van de katalysator, gebruik makend van kinetische mechanismen die zijn verkregen uit onder goed gedefinieerde omstandigheden gemeten experimentele gegevens. Het gedrag van een industriële autoutlaatgaskatalysator werd gesimuleerd onder procescondities die van belang zijn voor de opwarmperiode van de

Er werden twee voorbeelden gepresenteerd van optimalisatie van de prestatie van de katalysator door reactorsimulaties. Toepassing van Pt-belading volgens een degressief profiel doorheen de reactor kan de activiteit voor CO oxydatie vergroten, hetgeen een meer efficiënt gebruik van edelmetalen mogelijk maakt. Ook toevoeging van lucht aan het uitlaatgas stroomopwaarts van de katalysator kan de CO conversie vergroten na een koude start, vooropgesteld dat het massadebiet van de lucht nauwgezet wordt aangepast aan de temperatuur van het uitlaatgas.
CONTENTS

SUMMARY/SAMENVATTNING 3

NOTATION 13

1 | INTRODUCTION 17

2 | EXPERIMENTAL EQUIPMENT AND PROCEDURES 25

2.1 Introduction 25
2.2 Reactor design 26
2.3 Experimental set-up 31
2.4 Conversion and net production rate 35
2.5 Catalyst preparation, characterisation and pretreatment 36
Appendix I Transport coefficients 42
Appendix II Evaluation of observed CO₂ production rates 45

3 | KINETICS OF CO OXIDATION OVER Pt/γ-Al₂O₃ 47

3.1 Introduction 47
3.2 Experimental 49
3.3 Influence of process variables on CO₂ production rate 53
3.4 Kinetic model development for CO oxidation 57
3.5 A priori values of kinetic parameters 63
3.6 Kinetic model selection and discussion 65
3.7 Conclusions 73
Appendix III Evaluation of observed CO₂ production rates 77
4 | KINETICS OF CO OXIDATION OVER A COMMERCIAL THREE-WAY CATALYST

4.1 Introduction 79
4.2 Experimental 81
4.3 Results 84
4.3.1 Chemisorption 84
4.3.2 Effect of ceria on the oxidation of CO over \( \gamma \)-Al\(_2\)O\(_3\) supported Pt, Rh and Pt/Rh catalysts 86
4.3.3 Influence of process variables on CO\(_2\) production rate using a commercial Pt/Rh/CeO\(_2\)/Al\(_2\)O\(_3\) catalyst 88
4.3.4 Step changes in isotopic compositions using a Pt/Rh/CeO\(_2\)/\( \gamma \)-Al\(_2\)O\(_3\) catalyst 92
4.4 Discussion 95
4.5 Conclusions 101

5 | EXPERIMENTAL SET-UP FOR INVESTIGATION OF FORCED CONCENTRATION CYCLING

5.1 Introduction 105
5.2 Experimental 108
5.3 Results and discussion 111
5.4 Conclusions 114

6 | SIMULATION OF AN INDUSTRIAL AUTOMOTIVE THREE-WAY CONVERTER

6.1 Introduction 117
6.2 Model equations 118
6.3 Results and discussion 121
6.4 Conclusions 126

7 | GENERAL CONCLUSIONS 129
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
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<td>$A$</td>
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<tr>
<td>$R_v$</td>
<td>volumetric production rate</td>
<td>$mol \cdot kg_{c}^{-1} \cdot s^{-1}$</td>
</tr>
<tr>
<td>$R_w$</td>
<td>specific production rate</td>
<td>-</td>
</tr>
<tr>
<td>$s$</td>
<td>standard deviation</td>
<td>-</td>
</tr>
<tr>
<td>$S$</td>
<td>objective function</td>
<td>-</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
<td>$K$</td>
</tr>
<tr>
<td>$u_s$</td>
<td>superficial velocity</td>
<td>$m^3 \cdot g \cdot m^{-2} \cdot s^{-1}$</td>
</tr>
<tr>
<td>$v$</td>
<td>diffusion volume</td>
<td>$m^3 \cdot mol^{-1}$</td>
</tr>
<tr>
<td>$v$</td>
<td>specific volume</td>
<td>$m^3 \cdot kg_{c}^{-1}$</td>
</tr>
<tr>
<td>$w$</td>
<td>catalyst metal loading</td>
<td>$kg_{metal} \cdot kg_{c}^{-1}$</td>
</tr>
<tr>
<td>$W$</td>
<td>catalyst mass</td>
<td>-</td>
</tr>
<tr>
<td>$x$</td>
<td>vector of process conditions</td>
<td>-</td>
</tr>
<tr>
<td>$X$</td>
<td>fractional conversion</td>
<td>-</td>
</tr>
<tr>
<td>$y$</td>
<td>mole fraction</td>
<td>-</td>
</tr>
<tr>
<td>$*$</td>
<td>vacant noble metal surface site</td>
<td>-</td>
</tr>
<tr>
<td>$s$</td>
<td>vacant support site</td>
<td>-</td>
</tr>
<tr>
<td>$^*$</td>
<td>rate-determining step</td>
<td>-</td>
</tr>
<tr>
<td>$O$</td>
<td>step at quasi-equilibrium</td>
<td>-</td>
</tr>
</tbody>
</table>

**Greek symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>heat transfer coefficient</td>
<td>$W \cdot m^{-2} \cdot K^{-1}$</td>
</tr>
<tr>
<td>$\alpha_r$</td>
<td>radiation coefficient</td>
<td>$W \cdot m^{-2} \cdot K^{-1}$</td>
</tr>
</tbody>
</table>
\( \beta \)
- geometry factor

\( \vec{\beta} \)
- vector of kinetic parameters

\( \delta_p \)
- normalized film thickness

\( \epsilon_b \)
- catalyst bed void fraction

\( \epsilon_p \)
- catalyst pellet void fraction

\( \epsilon_R \)
- monolith converter void fraction

\( \eta \)
- effectiveness factor

\( \theta \)
- fractional surface coverage

\( \lambda \)
- thermal conductivity

\( \mu \)
- dynamic viscosity

\( \nu \)
- atomic and structural volume increment

\( \xi \)
- dimensionless pellet coordinate

\( \nu \)
- stoichiometric coefficient

\( \rho \)
- density

\( \sigma \)
- stoichiometric number

\( \sigma \)
- atomic surface area

\( \tau \)
- tortuosity;

\( \tau \)
- average surface residence time

\( \phi \)
- Weisz modulus

\( \Phi \)
- Thiele modulus

\( \zeta \)
- molar flux

Subscripts

a
- activation

ads
- adsorption

b
- bulk; catalyst bed

c
- catalyst

des
- desorption

dis
- dissociation

e
- effective

ER
- Eley-Rideal

g
- gas

i
- with respect to component i; inner

LH
- Langmuir-Hinshelwood

p
- catalyst pellet

pore
- with respect to catalyst pellet pore

r
- radial; radiation; reaction

R
- reactor

s
- surface; solid; superficial
$t$ reactor tube; total
$v$ volumetric; with respect to void phase
$w$ specific; reactor wall
$0$ initial conditions; standard

Superscripts

0 static; standard; under reference conditions
ads adsorption
b backward
des desorption
dis dissociation
f forward
obs observed
Introduction

Background

Automotive exhaust catalysis started to be an important industrial process after the well known American Clean Air Act amendments were effectuated in the early seventies. Ever since, the emission standards have become more stringent, forcing car and catalyst manufacturers towards novel technologies. The result of these efforts is illustrated by the emission of hydrocarbons by the average new car in the USA, typically 0.3 g per mile as compared to over 10 g per mile prior to legislation.

The impact automotive emission legislation has had on the environment may be surpassed by the tremendous impact on industry. In an early stage the dominant factor was confusion, both technologically and logistically (Libby, 1973). The technological confusion was caused by early attempts of the California State Air Resources Board to restrict CO and hydrocarbons exhaust output. The technological answer to these provisions was a slight leaning of the air and fuel mixture, which, in turn, caused an increase in NO emissions (Wei, 1975). Another technological measure was recalibration of engines in combination with exhaust gas recirculation in order to reduce pollution. These measures, however, caused worse fuel economy, so after the 1973 oil crisis they were abandoned. Logistic confusion emerged when authorities realised approximately ten to twenty million cars would have to be fitted with catalytic converters annually, which meant a new industry had to be set up which would directly be one of the major catalyst industries.

Since 1977 every new car sold in the USA has been fitted with a catalytic converter, so one of the most important political and technological decisions of the last thirty years
succeeded. Technological evolution has led to the present state of the art combination of a multi-point fuel injection system and a closed loop controlled three-way catalyst. Logistical problems have been overcome, too: in 1989 one of the major automotive catalyst manufacturers, AC Rochester, sold their hundred-millionth converter.

Driving forces for research on automotive catalysts

Past to present

The driving force for research on automotive catalysts has been manifold. Two main issues have always controlled research in this field: having to meet growingly strict emission standards as economically as possible, and the pursuit of non-noble metal catalytic materials. The former is illustrated by Table 1.1 in which the evolution of hazardous exhaust emission reduction is shown for a typical small car in the USA, except for California.

The latter issue used to be strategically important because the western world had once more become dependent on foreign sources, namely South Africa and the USSR. Figure 1.1 shows the forecasted platinum and rhodium supplies in 1994 as an example. Relaxation of international relationships may have taken away the justification of this concern, but the next problem was the gross availability of platinum and especially rhodium. In 1994 the automotive sector was responsible for 35% and 91%, respectively, of the net world demand (Figure 1.2). However, the R/P ratio for noble metals, which is the ratio of the proven reserves and the present annual consumption rate (Meadows, 1974) stood at 250 to 400 years in 1990 (Steel, 1991). In 1987 the R/P ratios for oil and natural gas stood at approximately 40 and 60 years, respectively (British Petroleum, 1988), so it

### Table 1.1

*Evolution of exhaust management for a typical small car in the USA except for California.*

(Hofbauer and Thoms, 1984)

<table>
<thead>
<tr>
<th>Limits</th>
<th>Model year</th>
<th>Fuel supply</th>
<th>Cat type</th>
<th>Cells /in²</th>
<th>SAS EGR</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx</td>
<td>75</td>
<td>O</td>
<td>200</td>
<td>M Y</td>
<td></td>
</tr>
<tr>
<td>76</td>
<td></td>
<td>O</td>
<td>200</td>
<td>M Y</td>
<td></td>
</tr>
<tr>
<td>77</td>
<td></td>
<td>F I</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>78</td>
<td></td>
<td>C</td>
<td>0 O+ 300</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>79</td>
<td></td>
<td>T</td>
<td>300</td>
<td>N</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td></td>
<td>F I</td>
<td>T+O 300</td>
<td>Y</td>
<td></td>
</tr>
<tr>
<td>81</td>
<td></td>
<td>T+O 800</td>
<td></td>
<td>N Y</td>
<td></td>
</tr>
<tr>
<td>82</td>
<td></td>
<td>T+O 300/400</td>
<td></td>
<td>N Y</td>
<td></td>
</tr>
<tr>
<td>83</td>
<td></td>
<td>T+O 800/400</td>
<td></td>
<td>N Y</td>
<td></td>
</tr>
<tr>
<td>84</td>
<td></td>
<td>T+O 300/400</td>
<td></td>
<td>N Y</td>
<td></td>
</tr>
</tbody>
</table>

Figure 1.1

*Forecasted net platinum (upper) and rhodium (lower) supplies in 1994 (Cowley, 1994).*
may be concluded that the reserves of noble metals will outlive the use of fossil fuels in cars.

An important driving force to decrease the amount of noble metals required has always been the effect of the noble metals market price on the total manufacturing costs of converters. At present, the estimated value of noble metals in a typical converter amounts to US$ 30 at a total sale price of approximately US$ 800 (Vonkeman, 1990). This relatively small contribution to the total price is caused by the high price of the exhaust composition control unit. Nevertheless, considering the massive amounts of catalytic converters being produced, estimated to be 50 millions per year by the year 2000, this economic factor will continue to be a driving force for catalyst research (Engler et al, 1994).

In 1973 it has been forecasted that platinum would only have to be used temporarily until more readily available materials would be discovered (Libby, 1973), however, nowadays the majority of researchers seem to have accepted that noble metals are essential in automotive exhaust catalysts.

**Present and future**

Contemporary driving forces for automotive catalyst research are induced by the latest Clean Air Act provisions, especially the Californian. These new measures will, via Transitional Low Emission Vehicles (TLEV), lead to so-called Low Emission Vehicles (LEV) and Ultra Low Emission Vehicles (ULEV). Although engine construction improvements are expected to facilitate meeting these standard with the present catalyst technology (Eyzat, 1994), hydrocarbon and nitrogen oxides emission standards are so tight that new catalyst developments are necessary (Ball and Jacque, 1994), see Table 1.2.

Because the majority of poisonous emissions occur before the catalyst has reached the light-off temperature (Rijkeboer, 1991), which is the temperature required for 50% conversion of pollutants, various strategies are presently in focus. The first option, fitting cars with externally heated converters, does indeed reduce CO and hydrocarbon emissions, the drawback being the high costs and potential dangers of applying large electrical currents. A second option seems more readily feasible: additional installation of so-called close coupled converters, which are small converters located upstream of the three-way converter, typically within 0.5 m from the exhaust manifold (Gulati et al., 1994; Bali and Jacque, 1994). The obvious advantage is the fact that light-off temperature is reached sooner.

These new catalysts developments require improved thermal stability of both noble metal and support, a reason for emission engineers to re-evaluate the use of Pd, which features both

---

**Table 1.2**

<table>
<thead>
<tr>
<th>Year and standard</th>
<th>Pollutant, g mile(^{-1})</th>
<th>NO(_x)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1900 U.S.</td>
<td>0.41 3.4</td>
<td>1.0</td>
</tr>
<tr>
<td>1994 U.S</td>
<td>0.25 3.4</td>
<td>0.40</td>
</tr>
<tr>
<td>1993 Calif.</td>
<td>0.25 3.4</td>
<td>0.40</td>
</tr>
<tr>
<td>1994 TLEV</td>
<td>0.125 3.4</td>
<td>0.40</td>
</tr>
<tr>
<td>1997 LEV</td>
<td>0.075 3.4</td>
<td>0.20</td>
</tr>
<tr>
<td>1997- ULEV</td>
<td>0.040 1.7</td>
<td>0.20</td>
</tr>
</tbody>
</table>
better light-off performance (Beek and Sommers, 1994) and better thermal stability as compared to Pt and Rh, but only in combination with excellent air to fuel ratio control (Taylor, 1994). A surprising disadvantage has been found for this type of catalysts: reduction of nitrogen oxides in the three-way converter may be impaired because, after passing through the close coupled converter, the exhaust gas contains too small amounts of reductants. Studies of other, highly selective reduction catalysts like Pt/ZSM5 are already in progress (Kharas et al., 1994).

Another important incentive for using Pd is that it results in improved catalyst manufacturer flexibility. At present, Rh is necessary for NO\textsubscript{x} reduction, resulting in a catalyst manufacturer dependence on the Rh market. The rhodium to platinum ratio in automotive catalysts exceeds by far the mining ratio (1/5 and 1/19 respectively) while the automotive sector virtually is the sole consumer of Rh. Hence, if the platinum market demand does not keep pace with the rhodium demand, rhodium might be in short supply, regardless of the known reserves. The fluctuation of the Rh price when European car manufacturers started mass producing cars fitted with three-way converters in 1990 is illustrative: from a stable US$ 1300 per troy ounce in 1988 the Rh market price exploded to $ 7600 per troy ounce in summer, 1990, stabilising at $4500 per troy ounce later that year. Increased manufacturer flexibility results in a better spread risk against fluctuations of market prices.

The role of kinetic research

Throughout the years, new emission standards could often be met by a series of engine related and catalyst improvements, as was shown in Table 1.1. Optimisation of existing technologies in order to comply with more stringent legislation is facilitated by knowledge of the intrinsic kinetics of reactions occurring in automotive catalysts. By addressing phenomenological observations in terms of a mathematical description of elementary reaction steps the performance of converters can be simulated under any set of reaction conditions, giving insight into the intricate processes taking place as a function of process conditions (Lie et al., 1993, Nievergeld, 1994).

Furthermore, from knowledge of the reaction kinetics shortcomings of presently used materials can be pin-pointed so catalysts may be optimised by adding specific substances to
attain the desired performance. An example has been recently published by researchers from the Engelhard corporation (Dettling et al., 1994). Although their Strategic Material Architecture at Reaction Temperatures (SMART) approach does not include a full kinetic analysis, it does show the potential of tailor-made catalyst design.

Finally, once the complex kinetics of the appropriate reactions are known a novel issue may come into focus: development of feed forward air to fuel ratio controlling devices based on kinetic models. These controllers, which allow fine tuning of the air to fuel ratio could be implemented in combination with current state of the art feed forward air to fuel ratio controllers. The latter contain a mapping of characteristic parameters for optimising the fuel combustion process but only allow coarse tuning as far as emissions are concerned. However, this development will not take place comprehensively in the near future because of the lack of knowledge of the reaction kinetics under a wide range of operating conditions encountered in practical use.

Scope of this thesis

CO oxidation over noble metal catalysts has been widely studied during the last decades, an extensive review has been published by Razon and Schmitz, (1986). However, hardly any studies have been provided in which the kinetics were described by elementary step modelling using intrinsic kinetic rate data. Since CO oxidation by oxygen in the presence of steam is one of the most important reactions occurring in three-way catalysts, the kinetics of this reaction are evaluated under experimental conditions relevant to practical use, using a Pt/γ-Al₂O₃ catalyst. Because of the importance of low temperature emissions this study was carried out at temperatures well below light-off.

The performance of ceria containing Pt/Rh three-way catalysts has received much attention recently (Crucq, 1990); the reaction mechanism for CO oxidation over these catalysts is still debated. For that reason this mechanism is addressed, in particular the role of steam in the presence of cerium oxide. Part of this investigation is aimed at assignment of the major source of oxygen in CO oxidation by means of isotope kinetic experiments.

Since the present state of the art exhaust gas composition control loop is a feed back loop, feed concentration oscillations occur in practical catalysts (Taylor and Sinkevitch, 1983). The effects of these forced concentration cycles may be either advantageous, neutral, or detrimental to CO conversion performance, depending on the operating conditions (Schlatter et al., 1983; Cho and West, 1986; Graham and Lynch, 1990). In order to allow evaluation of these effects a novel reactor set-up has been designed, and the feasibility of frequency-response analysis as a tool in kinetic modelling of CO oxidation is discussed.

As a demonstration of the merits of kinetic research, an industrial monolith converter is simulated, which includes setting up a reactor model and incorporating the kinetic model developed for CO oxidation over a supported platinum catalyst.
References

-Ball D.J., Jacque E., 'A palladium front brick study,' Preprints of the Third International Congress on Catalysis and Automotive Pollution Control (CaPoC3), 137-146, 1994.


-Eyzat P., 'Internal combustion engines probable evolutions and trends,' Preprints of the Third International Congress on Catalysis and Automotive Pollution Control (CaPoC3), 5-15, 1994.


INTRODUCTION

EXPERIMENTAL EQUIPMENT AND PROCEDURES

2.1 Introduction

The experimental set-up has been designed to permit kinetic experiments under operating conditions typical for automotive exhaust catalysts. These conditions apply to temperature, reactant partial pressure and space-time. Based on literature data regarding exhaust gas composition (Taylor and Sinkevitch, 1983) and space-time yields (Herz and Marin, 1980) in combination with the minimum amount of catalyst experimentally feasible, estimated to $10^4$ kg, the boundary conditions for the set-up dimensions have been determined. In order to measure intrinsic kinetics, i.e., kinetics solely determined by chemical processes, the absence of significant physical transport or transfer resistances under the operating conditions applied is imperative. Reactors may be designed as to minimise the influence of physical transport phenomena on the kinetic data measured, by application of the appropriate design criteria.

The experiments described in this thesis can be divided into three groups: steady state experiments, steady state isotopic transient experiments and forced concentration cycling experiments. All experiments have been carried out using continuous flow laboratory fixed bed reactors; both steady state and steady state isotopic transient experiments have been performed using the reactor described in this chapter. Concentration cycling experiments require special attention regarding back-mixing of reactant and product gases. Moreover, desired real-time chemical analysis of reactor feed and effluent demands a different means of gas sampling as compared to steady state experiments. In order to enable forced concentration cycling experiments, a novel laboratory reactor has been designed which is described in Chapter 5.
2.2 Reactor design

In order to measure intrinsic kinetics, development of significant temperature gradients and concentration gradients must be avoided. Using a fixed bed reactor two aspects can be identified: gradients regarding the catalyst bed -gradients on catalyst bed scale- and gradients related to a catalyst pellet, or gradients on catalyst pellet scale.

For a given set of operating conditions, the magnitude of these gradients is a function of the design parameters, which are: diameter and length of the catalyst bed, diameter of catalyst pellets, the catalyst bed dilution degree and the type of catalyst diluent. Criteria validating negligibility of gradients during steady state operation have been, in part, taken from literature. These criteria relate the design parameters to the kinetic properties of the reaction considered and to the physical properties of the catalyst bed and the reaction medium. Transport parameters required for application of the criteria are specified in Appendix I.

Physical properties have been taken from Yaws (1976), Weast (1987) and Reid et al. (1988).

**Gradients on catalyst bed scale**

**Pressure drop**

Allowing a maximum relative pressure drop of 3% and using Ergun’s equation for pressure drop in a fixed bed reactor the criterion expressed by Eq. 2.1 is obtained.

\[
\frac{150 (1 - \varepsilon_b) \mu u_z L}{p_0 \varepsilon_b^3 d_p^2} + \frac{1.75 (1 - \varepsilon_b) \rho \varepsilon_b u_z^2 L}{p_0 \varepsilon_b^3 d_p} \leq 0.03 
\]

(2.1)

*Axial and radial concentration gradients* are irrelevant if the reactor is operated differentially. A differential reactor is defined as a reactor in which sufficiently low conversions are realised for its influence on the measured production rate to be negligible. This results in a uniform production rate throughout the reactor which can be calculated from Eq. 2.2.

\[
-R_{w,i} = \frac{X_i}{W / F_{i0}} 
\]

(2.2)

The benefits of differential operation as compared to an integral reactor are i) straightforward calculation of production rates from experimental conversion data, ii) enhanced isothermicity because of reduced specific heat production, iii) the flow pattern in the reactor is irrelevant,
hence, diluting the catalyst with an inert diluent does not affect conversion of reactants. Potential drawbacks are a relatively large measurement error and rather difficult determination of the range of differential operating conditions. Because of the potential benefits the reactor has been designed to allow differential operation under the desired conditions.

Plug flow is important in steady state isotopic transient experiments and forced concentration cycling experiments. Therefore the reactor has been designed in order to obey the plug flow criteria according to Mears (1971a).

\[
\frac{d_t}{d_p} > 10 \tag{2.3}
\]

\[
\frac{L}{d_p} > 50 \tag{2.4}
\]

In Eq. 2.5 (Mears, 1971b) a criterion for the absence of significant radial temperature gradients is represented. If this criterion is satisfied, the maximum relative difference in production rates due to a radial temperature gradient does not exceed 5%.

\[
\frac{\Delta H_t^0}{r_s d_t^2 (1-e_b)(1-b)} < \frac{1.6 \frac{RT}{E_b}}{1 + \frac{8 \lambda_c}{\alpha_w d_t}} \tag{2.5}
\]

In a fixed bed reactor axial temperature gradients are determined by the adiabatic temperature rise and the rate of axial heat transport, assuming a uniform axial temperature profile of the external reactor wall. Because the reactor is designed as a differential reactor, isothermicity is readily achieved. In order to verify isothermal operation the axial temperature profile was measured during the experiments by shifting a thermocouple through a tube along the axis of the catalyst bed.
Gradients on catalyst pellet scale

Concentration gradients on catalyst pellet scale are caused by two processes, these are gas film resistance, referred to as external diffusion resistance, and pore diffusion resistance, referred to as internal diffusion resistance. External diffusion resistance occurs when reactants diffuse from the bulk of the fluid to the exterior surface of a pellet. For mass transfer and reaction acting in series, the concentration gradient is calculated according to Eq. 2.6:

\[
R_{w,i} = k_e a_s (C_{b,i} - C_{s,i})
\]

assuming equimolar counterdiffusion into and out of the pores of the pellet. The influence of mass transfer may be neglected if the concentration gradient does not exceed 3% of the bulk concentration.

The influence on the intrinsic production rate of internal diffusion resistance is expressed as the effectiveness factor \( \eta \), defined as the ratio of the actual volume averaged reaction rate within the pellet and the intrinsic rate, which is the rate corresponding to the reaction conditions at the external surface of the pellet. The effectiveness factor \( \eta \) can be calculated from the Thiele modulus \( \phi \). Considering an irreversible reaction of reactant \( i \) with partial reaction order \( n \), diffusing into a spherical porous catalyst particle, \( \phi \) is calculated according to Eq. 2.7:

\[
\phi = \frac{d_p}{6} \left[ \frac{n + 1}{2} \frac{k_s C_i^{n-1}}{D_e} \right] \quad n > -1
\]

On expressing Eq. 2.7 in measurable quantities the Weisz modulus \( \Phi \) is obtained, and the resulting criterion is expressed as:

\[
\Phi = \eta \phi^2 = \frac{n + 1}{2} \left( \frac{d_p}{6} \right)^2 \frac{R_{v,i}}{D_e C_{s,i}} < 0.25 \quad n > -1
\]

If \( \Phi \) is smaller than 0.25 the effectiveness factor is greater than 0.95, hence, pore diffusion resistance does not significantly affect the intrinsic production rate.

Temperature gradients on catalyst pellet scale are treated analogous to concentration gradients. For a stoichiometrically single reaction, heat production and transfer acting in series the enthalpy balance is:
assuming an isothermal catalyst pellet. According to Mears (1971b) the influence of heat transfer resistance on the net production rate may be neglected if

\[
\left| \frac{\Delta H^0_T}{\alpha T_b} \right| \frac{r_w \rho_s d_p}{\alpha T_b} < 0.3 \frac{R T_b}{E_a}
\]  

(2.10)

Intraparticle temperature gradients can be neglected if the following criterion is satisfied (Mears, 1971b):

\[
\left| \frac{\Delta H^0_T}{\lambda_p T_b} \right| \frac{r_v d_p^2}{\lambda_p T_b} < 3.0 \frac{R T_b}{E_a}
\]

(2.11)

Design criteria and negative partial reaction orders

Care must be taken in case of negative reaction orders: in general only positive order reactions may be treated using Eqs. 2.7 to 2.11. In case of a negative reaction order pore diffusion resistance will enhance the production rate as long as the reaction is not stoichiometrically limited. Moreover, this rate enhancement may result in an increase of the temperature gradient over the external gas film, generating still higher rates. Hence, negative order kinetics tend to self-amplification whereas in case of positive order kinetics mass and heat transport limitations counteract. Smith et al. (1975) numerically solved enthalpy and mass balances for CO oxidation over a Pt catalyst using a spherical catalyst particle. The rate equation used features a negative partial reaction order for CO for high CO concentrations, see Eq. 2.12.

\[
R_v = \frac{k C_{CO}}{\left(1 + K_{ads}^{CO} C_{CO}\right)^2}
\]

(2.12)

As long as isothermicity is guaranteed, the effectiveness factor does not appreciably differ from unity if $\phi \leq 10$, indicating a substantial expansion of the criterion in Eq. 2.8 which corresponds to $\phi \leq 0.5$. If significant temperature gradients exist, however, the effectiveness factor will increase at lower values of $\phi$, as opposed to positive reaction order behaviour. Under conditions typical for automotive catalysts these temperature gradients are not likely to occur at temperatures applied in this work.

In CO oxidation the kinetic rate equation is likely to contain a positive partial reaction order in $O_2$ and a negative one in CO, see Chapter 3. Although, obviously, the stoichio-
metrically limiting component should be addressed in evaluation of pore diffusion resistance, the component featuring a positive partial reaction order will appear the more critical. If the reactor feed contains a stoichiometric mixture of reactants, deviations from $\eta \approx 1$ related to a single component are counteracted by the presence of the second component.

Reactor dimensions

In conclusion, reactor design for steady state operation according to criteria valid for first order kinetics seems safe. The resulting reactor is shown schematically in Figure 2.1. To satisfy all necessary criteria over a wide range of operating conditions requires iterative optimisation of the design parameters because the reactor design is a compromise between counteracting criteria, e.g., decreasing the catalyst pellet diameter reduces heat transfer resistance and internal diffusion resistance but it increases pressure drop. Pressure drop may be reduced by increasing the reactor diameter which may, in turn, cause a radial temperature gradient.

From the discussion in this section it is clear that during kinetic measurements the above criteria should be verified for each set of operating conditions. On-line verification has been carried out during kinetic experiments by means of a spreadsheet program containing the equations for the design criteria and correlations for physical properties required. After changing the operating conditions the criteria were verified using the CO$_2$ production rate measured under those conditions. Only intrinsic rates were accepted. An example of the evaluation of an observed CO$_2$ production rate is shown in Appendix II.

![Schematic of the reactor used in steady state and steady state isotopic transient experiments. Dimensions are in millimetres.](image)
2.3 Experimental set-up

The experimental set-up outlined in Figure 2.2 consists of a feed section, a reactor section and an on-line gas analysis section.

![Outline of the experimental set-up.](image)

**Feed section**

The feed section contains two duplicate gas blending systems to allow generation of two feed streams. In steady state experiments only one gas blending system is used. In steady state isotopic transient experiments the feed streams only differ as far as the isotopic composition is concerned, whereas during forced concentration cycling experiments the composition of the feed streams are different while the total molar flow rate of both feed streams remains equal. Each gas blending system includes a series of thermal gas mass flow controllers (Sierra Side=Trak 840D) and a HPLC pump (Pharmacia LKB 2150-0010) to feed water to an evaporator located downstream of the flow controllers. Upstream of the flow controllers each gas supply line is secured by an electromagnetic valve (Asco) actuated by a
programmable logic controller (PLC, Siemens). Downstream of the flow controllers the gases pass through a one-way valve prior to mixing, while an adjustable pressure relieving valve is installed to prevent unanticipated pressure build-up in the set-up. In order to prevent water condensation all lines and devices downstream of the water evaporators, but upstream of the steam condensers, are heated to 350 K.

Because accurate, reproducible feeding of steam was required, much effort has been spent in designing proper evaporators; the principle applied is shown in Figure 2.3. Water is fed to the evaporator through a capillary located in the axis of the feed gas line. At the end of the capillary the gas feed line is constricted, thus creating a high gas velocity and, consequently, a lower pressure at the outlet of the capillary. By tuning the location of the capillary relative to the gas feed line a nozzle was created yielding a fine spray of water. The evaporators are heated by a tubular oven, the temperature at the evaporator wall, directly downstream of the nozzle, is controlled by a PID controller (West 2200). By heating the evaporator to 363 K a steady steam flow could be established, the standard deviation in the steam flow rate, as determined by MS analysis, typically being smaller than 5%. The lower halves of the evaporators are filled with glass beads in order to prevent occasional drops of water from directly entering the reactor section. The upper half does not contain beads as to allow jet development from the nozzle.

After passing through a valve arrangement the feed stream enters the reactor section. The valve arrangement consists of four fast acting miniature two-way solenoid valves (Asco Angar 008, time to open or close: 3-5 ms), actuated by synchronised digital timers for concentration cycling use or by the PLC during steady state isotopic transient experiments. By opening the valves two by two one feed stream is directed to the reactor while the other one is by-passed to the exhaust. For more details about transient operation and the pressure control provisions involved see Chapter 5.

Reactor section

The reactor section consists of a tubular preheater and a reactor which is contained in a cylindrical oven. The reactor employed is a stainless steel laboratory reactor containing the catalyst bed as shown in Figure 2.1. Herz (1981), Hecker and Bell (1983) and Oh (1990) applied aluminum constructions in order to minimise catalytic action of the reactor wall: aluminum is easily covered with an alumina layer upon exposition to oxygen. However, under the operating
conditions applied in this work, no significant difference was found between rate data measured with stainless steel or aluminum reactors. Because of mechanical difficulties encountered in stainless steel to aluminum connections, the majority of experiments were carried out using a stainless steel reactor.

The catalyst bed, retained by a sintered quartz plate, is diluted with non-porous $\alpha$-$\text{Al}_2\text{O}_3$ particles of the same average diameter as the catalyst particles in order to minimise temperature gradients in the reactor and to allow differential operation of the reactor. A typical catalyst bed contained 0.200 g catalyst and 1.800 g diluent. The reactor inlet and outlet are filled with $\alpha$-$\text{Al}_2\text{O}_3$ beads, 1 mm in diameter, in order to maintain an isothermal catalyst bed and to enhance radial distribution of the inlet stream.

The reactor is heated by two infra red radiators (Heraeus ZKB 600/80G) placed in line with the reactor, each at 85 mm from the reactor wall, and reactor and radiators are surrounded by a polished stainless steel canister with an inner diameter of 250 mm. The radiators are connected to a PID controller (West 2800), the indicating thermocouple (Tempcontrol MTK-6-1xK) is attached to the centre of the outer reactor wall by means of a steel clip. Reactor pressure is controlled by a spring loaded back pressure controller (Tescom 44-4760) and measured downstream of the reactor using a pressure transducer in combination with a digital indicating device (Druck PTX 611 and DPI 262, respectively).

Methane, serving as an internal standard component for chemical analysis is added to the reactor effluent directly downstream of the reactor. Subsequently, a fraction of the effluent, typically 150 ml/min, is directed to the gas analysis section; the remaining stream is passed through a water cooled counter-current steam condenser (length = 500 mm; inner diameter = 50 mm; cooling surface area = 0.09 m$^2$) before being discharged to the exhaust line.

Gas analysis section

The on-line gas analysis section contains a gas chromatograph (Carlo Erba Instruments GC 8340) and a quadrupole mass spectrometer (VG Sensorlab 200D), both are connected to the reactor inlet and outlet lines via heated sample lines.

The gas chromatographic analysis has been designed to enable on-line quantitative analysis of $\text{H}_2$, $\text{N}_2$, $\text{CO}$, $\text{NO}$, $\text{O}_2$, $\text{CO}_2$ and $\text{N}_2\text{O}$ without interference of methane or steam. Separation of these components can be achieved using a Porapak Q column (length 6 m, particle diameter 0.15-0.18 mm) using 99.999% pure helium as carrier gas, in combination with a 500 $\mu$l sample loop. However, separ-
The quadrupole mass spectrometer has been used in three different modes. The first is monitoring the water signal at $m/e = 18$ in steady state experiments, the sole purpose being verification of the stability of the steam flow rate. The water signal has been measured relative to $m/e = 15$ of methane to compensate for potential changes in mass spectrometer sensitivity as a function of time. The second mode, during steady state isotopic transient experiments, is monitoring the evolution of isotopes after a step change in the feed gas isotope composition. Both modes have in common that no calibration of the mass spectrometer detector is required except for its sensitivity towards water. In the third mode, operated during forced concentration cycling experiments, calibration is necessary, this subject is treated in Chapter 5.

The quadrupole mass spectrometer is equipped with an enclosed ion source, a triple mass filter and a 240 l/s turbo molecular pump, backed by a rotary pump. The relatively large pumping capacity enhances helium, hydrogen and water pumping capabilities. Ion currents are analyzed by an off-axis secondary electron multiplier. Samples are pumped to the MS through a dual heated capillary inlet (fused silica, $L = 1.8$ m, $d_i = 0.32$ mm) connected to the vacuum system by means of a zero volume three-way valve. From the three-way valve a small fraction
is passed to the ion source through a Metrasil glass leak while the rest is vented via the backing pump.

Except for forced concentration cycling experiments, the mass spectrometer was connected to the GC sample line directly upstream of the Hayesep Q column. In this way both GC and MS acquired equally treated samples. Automated mass spectrometer control and data acquisition are performed using VG Sensorlab software installed on a dedicated 386DX personal computer.

2.4 Conversion and net production rate

In GC gas analysis, application of an internal standard allows quantification of flow rates of the product gas constituents by relating peak surface areas to the flow rate of the internal standard. The flow rates of H₂, O₂, CO and CO₂ at the reactor outlet are calculated according to:

\[ F_i = F_{CH_4} \frac{A_i}{A_{CH_4}} \frac{f_i}{f_{CH_4}} \]  

(2.13)

The calibration factors \( f_i \) accounting for different detector sensitivity towards different species, have been determined by analysing an external standard gas mixture containing a typical experimental reactor effluent composition. The calibration factors relative to methane for H₂, CO, O₂ and CO₂ amounted to 33.97, 0.854, 0.944 and 0.548, respectively. The flow rate of steam is determined by comparing its measured mass spectrometer intensity at \( m/e = 18 \) to that of methane at \( m/e = 15 \). The steam flow rate is calculated analogous to Eq. 2.13:

\[ F_{H_2O} = F_{CH_4} \frac{I_{H_2O}}{I_{CH_4}} \frac{f'_{H_2O}}{f'_{CH_4}} \]  

(2.14)

The calibration factor \( f'_{H_2O} \), typically amounting to 0.55, was calculated from analysing a mixture, generated by mass flow controllers and one of the HPLC pumps, containing steam and methane in helium.

In steady state isotopic transient experiments, the steady state flow rates of the reactor effluent components were determined by GC analysis according to Eq. 2.13 or, in the case of steam, by MS analysis (Eq. 2.14). On switching to the feed stream containing an isotopically labelled reactant, the evolution of this reactant and all products was monitored by MS. Because introduction of the isotopic transient does not perturb the steady state, measured MS intensities of isotope k of species i can be related to the flow rates determined from Eqs. 2.13 and 2.14 according to Eq. 2.15:

\[ F_{i,k} = \frac{I_{i,k}}{\sum I_{i}} F_{i,ss} \]  

(2.15)
Element balances of hydrogen, carbon and oxygen can now be verified by comparing the reactant inlet flow rates established with the mass flow controllers and the HPLC pumps, and the flow rates at the reactor outlet of all species calculated from Eqs. 2.13 and 2.14, and, in isotope experiments Eq. 2.15, according to:

\[
\text{Balance of isotope } k \text{ of element } j = \frac{\sum n_{k,i} F_i}{\sum n_{k,i} F_{i,0}}
\]  

(2.16)

where \( n_{k,i} \) is the number of atoms of isotope \( k \) of element \( j \) in species \( i \). The balances were closed within 5% for all experiments.

The fractional conversion of species \( i \) is defined as:

\[
X_i = \frac{F_{i,o} - F_i}{F_{i,o}}
\]  

(2.17)

and calculated according to the normalisation method, \textit{i.e.}, assuming 100% element balances. For CO oxidation by \( \text{O}_2 \) it can be shown that:

\[
X_{\text{CO}} = 1 - \frac{A_{\text{CO}} f_{\text{CO}}}{A_{\text{CO}} f_{\text{CO}} + A_{\text{CO}_2} f_{\text{CO}_2}}
\]  

(2.18)

and

\[
X_{\text{O}_2} = 1 - \frac{2 A_{\text{O}_2} f_{\text{O}_2}}{A_{\text{CO}_2} f_{\text{CO}_2} + 2 A_{\text{O}_2} f_{\text{O}_2}}
\]  

(2.19)

Net production rates are calculated according to Eq. 2.2,

\[-R_{w,i} = \frac{X_i}{W/F_{i,o}}
\]  

(2.2)

in which \( X_i \) is obtained from Eq. 2.18 and 2.19 for CO and \( \text{O}_2 \) respectively.

### 2.5 Catalyst preparation, characterisation and pretreatment

#### Preparation

Catalyst samples were supplied in powder form by Degussa A.G., the average powder diameter, as estimated from light diffusion experiments (Malvern), being 12 µm. Using this powder in a catalyst bed would result in significant pressure drop over the catalyst bed, hence, the powder needed to be pressed into larger pellets. At the same time, development of intra-particle concentration gradients needed be avoided. The optimum average particle diameter...
as calculated from Eqs. 2.1 and 2.8 was found to be 0.25 mm. In order to obtain this particle diameter, powder was pressed into pellets during 60 s, the pressure exerted being 1 GPa. Subsequently, the pellets were crushed and the desired fraction, $0.25 < d_p < 0.30$ mm, was collected.

Characterisation

Catalyst texture properties have been determined by static nitrogen physisorption and by mercury porosimetry measurements. The density of the porous particles has been calculated from the measured porosity and the density of non-porous solid support material, being either alumina or alumina and ceria. Texture properties have been determined for both powder and pellet samples, because mechanical pressing of the powder was considered likely to alter the pore volume and the pore radius distribution. In Figure 2.7 the cumulative specific pore volume is shown as a function of the pore radius. Mechanical pressing of the catalysts powder results in a severe loss of macro pore volume, however, this does not significantly alter the specific surface area.

The absence of Cu, Fe and Ni, potentially catalytically active contaminants in Pt/Al$_2$O$_3$ samples, was verified by atomic absorption spectroscopy, see Table 2.2. The catalyst Pt loading was measured using UV-spectroscopy, the result matching the manufacturer’s specifications. Since discrimination between platinum and rhodium was not possible using these techniques and considering the agreement between the measurements and the data supplied by Degussa no further chemical composition analysis was performed. For all Pt containing catalysts the Pt loading amounted to 0.398 w%, for the Rh containing catalysts the Rh loading amounted to 0.0798 w%.

The CO chemisorption characteristics of fresh catalyst samples were determined by static CO chemisorption measurements, using Micromeretics ASAP equipment. Prior to CO chemisorption the catalyst was pretreated in situ similarly to the samples used

<table>
<thead>
<tr>
<th>Task</th>
<th>Gas</th>
<th>Temperature /K</th>
<th>Time /ks</th>
</tr>
</thead>
<tbody>
<tr>
<td>purge</td>
<td>He</td>
<td>373</td>
<td>-</td>
</tr>
<tr>
<td>evacuation</td>
<td>-</td>
<td>373</td>
<td>1.8</td>
</tr>
<tr>
<td>oxidation</td>
<td>O$_2$/N$_2$ 20/80</td>
<td>373</td>
<td>0.6</td>
</tr>
<tr>
<td>oxidation</td>
<td>O$_2$/N$_2$ 20/80</td>
<td>773</td>
<td>3.6</td>
</tr>
<tr>
<td>evacuation</td>
<td>-</td>
<td>773</td>
<td>0.6</td>
</tr>
<tr>
<td>purge</td>
<td>He</td>
<td>773</td>
<td>1.8</td>
</tr>
<tr>
<td>evacuation</td>
<td>-</td>
<td>773</td>
<td>0.6</td>
</tr>
<tr>
<td>reduction</td>
<td>H$_2$</td>
<td>623</td>
<td>1.8</td>
</tr>
<tr>
<td>reduction</td>
<td>H$_2$</td>
<td>773</td>
<td>7.2</td>
</tr>
<tr>
<td>evacuation</td>
<td>-</td>
<td>773</td>
<td>1.8</td>
</tr>
<tr>
<td>purge</td>
<td>He</td>
<td>308</td>
<td>-</td>
</tr>
<tr>
<td>evacuation</td>
<td>-</td>
<td>308</td>
<td>1.8</td>
</tr>
<tr>
<td>leak test</td>
<td>-</td>
<td>308</td>
<td>-</td>
</tr>
<tr>
<td>chemisorption CO</td>
<td></td>
<td>308</td>
<td>20</td>
</tr>
</tbody>
</table>

Figure 2.6
Effect of mechanical pressing on the cumulative specific pore volume and the pore radii distribution. Pressure exerted: 1 Gpa.
for kinetic measurements, *vide infra*. Table 2.1 shows the CO chemisorption procedure; in this work this is referred to as the 'standard' CO chemisorption procedure. From the CO chemisorption capacities of the catalysts the fractions of exposed noble metal atoms were calculated using CO chemisorption stoichiometries of 1 CO per Pt atom and 2 CO atoms per Rh atom.

An attempt was made to obtain additional information with respect to Pt particle size from X-ray diffraction experiments, however, platinum particles were smaller than the detection limit of the equipment which is approximately 2 nm. Electron microscopy did not yield any additional information on the surface composition of the catalyst samples due to the very low noble metal loadings. Less than 1% of the catalyst surface is covered by noble metals, so the chance of focusing the electron microscope on a patch containing noble metal is quite small. Table 2.2 shows some relevant physico-chemical properties of the catalysts.

### Table 2.2

**Physico-chemical catalyst properties.**

<table>
<thead>
<tr>
<th>Support material type</th>
<th>γ-Al₂O₃ powder</th>
<th>γ-Al₂O₃ pellets</th>
<th>CeO₂/γ-Al₂O₃ powder</th>
<th>CeO₂/γ-Al₂O₃ pellets</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Texture properties</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \bar{r} ) /nm</td>
<td>5 / 800</td>
<td>5</td>
<td>5 / 800</td>
<td>10</td>
</tr>
<tr>
<td>( \sigma ) /m² kg⁻¹</td>
<td>193 10⁻³</td>
<td>225</td>
<td>157</td>
<td>125</td>
</tr>
<tr>
<td>( \nu_{\text{meso pore (BET)}} ) /m³ kg⁻¹</td>
<td>0.75 10⁻³</td>
<td>0.54 10⁻³</td>
<td>0.57 10⁻³</td>
<td>0.35 10⁻³</td>
</tr>
<tr>
<td>( \nu_{\text{micro pore (BET)}} ) /m³ kg⁻¹</td>
<td>1.30 10⁻³</td>
<td>-</td>
<td>1.14 10⁻³</td>
<td>-</td>
</tr>
<tr>
<td>( \nu_{\text{meso porosity (BET)}} ) /m³ kg⁻¹</td>
<td>2.05 10⁻³</td>
<td>0.54 10⁻³</td>
<td>1.71 10⁻³</td>
<td>0.35 10⁻³</td>
</tr>
<tr>
<td>( \nu_{\text{meso porosity (HgPor)}} ) /m³ kg⁻¹</td>
<td>1.74 10⁻³</td>
<td>0.44 10⁻³</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( \rho ) /kg m⁻³</td>
<td>430</td>
<td>1230</td>
<td>520</td>
<td>2280</td>
</tr>
<tr>
<td>( g_p ) /m³⁻¹ m⁻³</td>
<td>0.86</td>
<td>0.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Fraction exposed metal atoms</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( FE_{\text{Pt}} ) /mol, mol⁻¹</td>
<td>0.39</td>
<td>-</td>
<td>0.83</td>
<td>-</td>
</tr>
<tr>
<td>( FE_{\text{Rh}} ) /mol, mol⁻¹</td>
<td>0.52</td>
<td>-</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>( FE_{\text{Pt/Rh}} ) /mol, mol⁻¹</td>
<td>0.42</td>
<td>-</td>
<td>0.64</td>
<td>-</td>
</tr>
<tr>
<td><strong>Element analysis</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( w_{\text{Pt}} ) /mg kg⁻¹</td>
<td>3.98 10³</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( w_{\text{Rh}} ) /mg kg⁻¹</td>
<td>0.79 10³</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( w_{\text{Cu}} ) /mg kg⁻¹</td>
<td>20</td>
<td>20</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( w_{\text{Fe}} ) /mg kg⁻¹</td>
<td>100</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>( w_{\text{Ni}} ) /mg kg⁻¹</td>
<td>20</td>
<td>20</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

1) Volume averaged. Pores of the powder samples feature a bimodal distribution
2) Hgpor: mercury porosimetry
3) See Chapter 4 for details
From the fraction exposed noble metal atoms the concentration of active sites, in units of mol kg\(^{-1}\), can be calculated from Eq. 2.20, assuming each noble metal surface atom represents one active site.

\[ L_i = \frac{FEW}{M_{NM}} \]  

(2.20)

With \( L_i \), the turnover frequency, \( N \), in units of s\(^{-1}\), can be calculated from the net specific production rate \( R_w \), in units of mol kg\(^{-1}\) s\(^{-1}\), according to Eq. 2.20.

\[ N = \frac{R_w}{L_i} \]  

(2.21)

**Catalyst pretreatment**

In order to enable reproducible kinetic experiments an appropriate catalyst pretreatment procedure is important. Pretreatment procedures employed with supported noble metal catalysts found in literature are diverse: isothermal reduction in pure H\(_2\) (Herz, 1980, Yao and Yu Yao, 1984, Hepburn et al., 1991); or in diluted H\(_2\) streams (McCabe and Wong, 1989, Oh and Eickel, 1988); temperature programmed reduction in pure H\(_2\) (Muraki and Fujitani, 1986) or in diluted H\(_2\) streams (Anderson, 1991); reduction in pure H\(_2\) followed by oxidation in pure O\(_2\) (Schlatter and Chou, 1978, Otto et al., 1991); oxidation in diluted O\(_2\) followed by reduction in diluted H\(_2\) (Oh, 1990, Kellow and Wolf, 1990, Lööf et al., 1991). Some authors report reduction in CO (Cho et al., 1989) or oxidation in NO (Hecker and Bell, 1983), this type of pretreatment procedures is usually carried out specifically in order to study the transient behaviour of catalysts with pre-adsorbed reactants. Few explanations are given for the pretreatment procedures used; Otto et al. (1991) claim their procedure causes a higher fraction Pt atoms exposed as compared to procedures in which oxidation is followed by reduction.

The pretreatment procedure carried out, regardless of the amount of catalyst used, prior to the experiments described in this thesis is as follows. The catalyst is heated to 773 K in a steady flow of He. Then the catalyst is oxidised during 4 ks by a stream containing 25 vol% of O\(_2\). Next, the catalyst is kept under flowing He at 773 K for 2 ks in order to purge reversibly adsorbed oxygen, followed by reduction in a He stream containing 5 vol % H\(_2\) at 773 K for 8 ks. Finally, the catalyst is allowed to cool down to reaction temperature under a He stream. In Table 2.3 the experimental conditions during pretreatment are summarised.
Table 2.3
Experimental conditions during catalyst pretreatment.

<table>
<thead>
<tr>
<th>pretreatment phase</th>
<th>inlet flow rate mol s⁻¹</th>
<th>T ( \text{K} )</th>
<th>t ( \text{ks} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>He</td>
<td>O₂</td>
<td>H₂</td>
</tr>
<tr>
<td>heating</td>
<td>1.7 ( 10^3 )</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>oxidation</td>
<td>5.6 ( 10^4 )</td>
<td>1.4 ( 10^4 )</td>
<td>0</td>
</tr>
<tr>
<td>purge</td>
<td>1.7 ( 10^3 )</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>reduction</td>
<td>8.4 ( 10^4 )</td>
<td>0</td>
<td>4.4 ( 10^{-5} )</td>
</tr>
<tr>
<td>cooling</td>
<td>1.7 ( 10^3 )</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

References:


Appendix I

Transport coefficients

Diffusion coefficients

The effective diffusion coefficient within a porous particle is calculated according to the Bosanquet expression:

\[
\frac{1}{D_{e,i}} = \frac{\tau}{\varepsilon_p D_{m,i}} + \frac{\tau}{\varepsilon_p D_{K,i}} \tag{I.1}
\]

In all calculations the catalyst tortuosity was taken to be 3.0 m²/m² c.

The Knudsen diffusion coefficient is calculated according to:

\[
D_K = \frac{2}{3} \frac{8RT}{\pi M} \frac{1}{\bar{r}} \tag{I.2}
\]

The molecular diffusion coefficient for component i is calculated from the contributions of the binary molecular diffusion coefficients of i in a mixture containing n components:

\[
D_{m,i} = \left( \sum_{j=1}^{n} \frac{y_j}{D_{i,j}} \right)^{-1} \tag{I.3}
\]

in which the binary molecular diffusion coefficient can be calculated from the Füller-Schettler-Giddings correlation (Reid et al., 1988):

\[
D_{i,j} = \frac{3.16 \times 10^{-8} T^{1.75} \sqrt{M_i^{-1} + M_j^{-1}}}{p (v_i^{1/3} + v_j^{1/3})} \tag{I.4}
\]

where the diffusion volume \( v \) of a component consisting of \( n \) atoms can be calculated from the atomic and structural volume increment \( v \) according to:

\[
v_i = \sum_{j=1}^{n} v_j \tag{I.5}
\]

Since no substantial difference exists between the molecular diffusion coefficients of the
reactants in all equations a single value for $D_m$ has been adopted.

**Mass and heat transfer coefficients**

Mass and heat transfer coefficients can be calculated from the $j_D$ and $j_H$ factors for fixed bed reactors according to:

$$j_D = \frac{Sh}{Re_p Sc^{1/3}} = \frac{k_p d_p}{D_m Re_p Sc^{1/3}}$$  \hspace{1cm} (1.6)

$$j_H = \frac{Nu}{Re_p Pr^{1/3}} = \frac{\alpha d_p}{\lambda_p Re_p Pr^{1/3}}$$

Both $j$-factors can be deduced from correlations for fixed bed reactors found in literature. In this work the correlation of Hougen and Watson for the $j_D$-factor is used:

$$j_D = 1.66 Re_p^{-0.51}$$  \hspace{1cm} (I.7)

the Chilton-Colburn analogy between mass and heat transport, $j_D = j_H$, can only be applied under limited conditions, so a second correlation is used for determination of $j_H$ (de Acetis and Thodos, 1960):

$$j_H = \frac{1.1}{Re_p^{0.41} - 0.15}$$  \hspace{1cm} (I.8)

From Eqs. I.7 and I.8, for $8 < Re_p < 300$, which is reasonable for the experiments described in this thesis, the maximum relative variation between $j_D$ and $j_H$ amounts to 5%.

**Effective radial thermal conductivity**

Radial heat transport can be described by a two dimensional pseudo-homogeneous model, consisting of a static and a hydrodynamic part (Froment and Bischoff, 1990):

$$\lambda_{e,r} = \lambda_{e,r}^{0} + \frac{0.0029 Re_p}{1 + 46 \left( \frac{d_p}{d_t} \right)^2}$$  \hspace{1cm} (1.9)

The static effective radial thermal conductivity can be calculated from the model presented by Yagi and Kunii (Kulkarni and Doraissamy, 1980), in which transport by conduction and radiation through the void gas phase as well as through catalyst pellets is incorporated. In Eq. I.10 $\beta$ is a geometrical factor between 0.9 and 1. The normalised film thickness, $\delta_p$, is a function of $\lambda_e/\lambda_s$ and can be estimated graphically from the article cited. The radiation coefficients are calculated according to Eqs. I.11 and I.12.
\[ \frac{\lambda_{w}}{\lambda_b} = \varepsilon_b \left( 1 + \beta \frac{d_\varepsilon \alpha_w}{\lambda_b} \right) + \frac{\beta (1 - \varepsilon_b)}{\left[ \frac{1}{\delta_p} + \frac{\alpha_w d_p}{\lambda_b} \right]^{-1} + \delta_p \frac{\lambda_b}{\lambda_b}} \] (I.10)

\[ \alpha_{w,v} = \frac{2.27 \times 10^{-7}}{1 + \frac{\varepsilon_b (1 - \varepsilon)}{2 \varepsilon (1 - \varepsilon_b)}} T^3 \] (I.11)

\[ \alpha_{w,s} = \frac{2.27 \times 10^{-7}}{2 - \varepsilon} T^2 \] (I.12)

Heat transfer coefficient at reactor wall

The heat transfer coefficient at the reactor wall, \( \alpha_w \), is introduced in the two dimensional pseudo-homogeneous model for effective radial heat transport in order to allow for a radially invariant effective thermal conductivity. Analogous to the effective radial thermal conductivity, \( \alpha_w \) includes a static and a hydrodynamic contribution, and can be calculated according to (Froment and Bischoff, 1990):

\[ \alpha_w = 20 \frac{\lambda_{w}}{d_\varepsilon} + 0.0134 \frac{d_\varepsilon}{d_p} Re \] (I.13)

References

Appendix II

EVALUATION OF OBSERVED CO₂ PRODUCTION RATES

A spreadsheet program has been developed for on-line evaluation of observed CO₂ production rates. This spreadsheet contains a section in which the experimental conditions are defined, a data analysis section where the measured molar flow rates of reactants and products in the reactor effluent are used to calculate conversions and net CO₂ production rates, see section 2.4, and a section containing correlations for physical properties of the gas and the equations required for calculation of the criteria, as shown in section 2.2. The input quantities used for calculation of the transport coefficients specified in Appendix I are listed in Table II.1, where $E_a$ has been estimated from initial experiments.

The physical properties of the gas, the transport coefficients valid under these experimental conditions and the calculated observed net CO₂ production rates, assuming differential operation, are listed in Table II.2

| Table II.1: |
| Input quantities in evaluation of observed CO₂ production rate using a Pt/γ-Al₂O₃ catalyst. |

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th>Kinetic properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$</td>
<td>$X_{CO}$</td>
</tr>
<tr>
<td>503 K</td>
<td>3.45 %</td>
</tr>
<tr>
<td>$p$</td>
<td>$E_a$</td>
</tr>
<tr>
<td>110 kPa</td>
<td>$10^5$ J mol⁻¹</td>
</tr>
<tr>
<td>$P_{CO}$</td>
<td>$\Delta H_r$</td>
</tr>
<tr>
<td>2.2 kPa</td>
<td>$2.8 \times 10^5$ J mol⁻¹</td>
</tr>
<tr>
<td>$P_{CO}/P_{O_2}$</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>$W$</td>
<td></td>
</tr>
<tr>
<td>$2.0 \times 10^{-4}$ kg</td>
<td></td>
</tr>
<tr>
<td>$W/F_{CO_2}$</td>
<td></td>
</tr>
<tr>
<td>3.0 kg s mol⁻¹</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bed properties</th>
<th>Catalyst properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>$L_o$</td>
<td>$\rho_e$</td>
</tr>
<tr>
<td>$1.1 \times 10^{-2}$ m</td>
<td>1230 kg m⁻³</td>
</tr>
<tr>
<td>$d_b$</td>
<td>$d_e$</td>
</tr>
<tr>
<td>$1.3 \times 10^{-2}$ m</td>
<td>$2.75 \times 10^{-4}$ m</td>
</tr>
<tr>
<td>$e_b$</td>
<td>$e_c$</td>
</tr>
<tr>
<td>0.5 m³ g⁻¹ m⁻³</td>
<td>0.66 m³ m⁻³</td>
</tr>
<tr>
<td>$b$</td>
<td>$\lambda_c$</td>
</tr>
<tr>
<td>0.78 m³ net m⁻³</td>
<td>1.0 W m⁻¹ K⁻¹</td>
</tr>
<tr>
<td>$\lambda_b$</td>
<td>$\delta_e$</td>
</tr>
<tr>
<td>20.0 W m⁻¹ K⁻¹</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td>$\tau$</td>
</tr>
<tr>
<td></td>
<td>3.0 m² m⁻²</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta$</td>
<td></td>
</tr>
<tr>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>$\delta_e$</td>
<td></td>
</tr>
<tr>
<td>0.08</td>
<td></td>
</tr>
</tbody>
</table>
Table II.2
Physical properties of the gas, transport coefficients and observed CO₂ production rates.

<table>
<thead>
<tr>
<th>Physical properties of the gas</th>
<th>Dimensionless groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_p$</td>
<td>$\rho$</td>
</tr>
<tr>
<td>21.2 J mol⁻¹ K⁻¹</td>
<td>$1.33 \times 10^2$ kg m⁻³</td>
</tr>
<tr>
<td>$\lambda_s$</td>
<td>$M$</td>
</tr>
<tr>
<td>0.21 W m⁻³ K⁻¹</td>
<td>$5.04 \times 10^3$ kg mol⁻¹</td>
</tr>
<tr>
<td>$\mu$</td>
<td></td>
</tr>
<tr>
<td>$2.83 \times 10^{-5}$ kg m⁻³ s⁻¹</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Transport coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_m$</td>
</tr>
<tr>
<td>$4.52 \times 10^{-3}$ m² s⁻¹</td>
</tr>
<tr>
<td>$D_k$</td>
</tr>
<tr>
<td>$4.86 \times 10^{-4}$ m² s⁻¹</td>
</tr>
<tr>
<td>$D_T$</td>
</tr>
<tr>
<td>$9.42 \times 10^{-7}$ m³ s⁻¹</td>
</tr>
<tr>
<td>$\alpha_{av}$</td>
</tr>
<tr>
<td>$1.32$ W m⁻² K⁻¹</td>
</tr>
<tr>
<td>$\alpha_{av}$</td>
</tr>
<tr>
<td>$5.10$ W m⁻³ K⁻¹</td>
</tr>
<tr>
<td>$\lambda^{av}$</td>
</tr>
<tr>
<td>$1.32$ W m⁻¹ K⁻¹</td>
</tr>
<tr>
<td>$\alpha_w$</td>
</tr>
<tr>
<td>$2030$ W m⁻² K⁻¹</td>
</tr>
<tr>
<td>$\alpha$</td>
</tr>
<tr>
<td>$905$ W m⁻² K⁻¹</td>
</tr>
<tr>
<td>$k_s$</td>
</tr>
<tr>
<td>$0.52$ m s⁻¹</td>
</tr>
</tbody>
</table>

The criteria have been calculated using Tables II.1 and II.2. In Table II.3 the relative values of the criteria are shown; if the relative value does not exceed unity the criterion considered is satisfied. The only criterion which is not satisfied is the reactor length to catalyst pellet diameter ratio. The assumption of plug flow in the reactor, however, is valid because both top and bottom of the reactor are filled with non-porous alumina particles, resulting in an increased 'effective' hydrodynamic reactor length. Moreover, if the assumption of differential operation is valid, which is reasonable since $X_{CO}$ was determined to be 3.45 %, the presence of radial concentration gradients is irrelevant.

In conclusion, no significant gradients have developed under the conditions described, hence, the observed CO₂ production rate is intrinsic.

Table II.3
Relative value of the design criteria.

<table>
<thead>
<tr>
<th>Catalyst bed</th>
<th>Gradient</th>
<th>Equation</th>
<th>relative value criterion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure drop</td>
<td>2.1</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>Radial concentration gradient</td>
<td>2.2</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>Radial temperature gradient</td>
<td>2.4</td>
<td>0.69</td>
<td></td>
</tr>
<tr>
<td>External concentration gradient $O_2$</td>
<td>2.5</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>Internal concentration gradient $O_2$</td>
<td>2.8</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td>External temperature gradient</td>
<td>2.10</td>
<td>0.20</td>
<td></td>
</tr>
<tr>
<td>Internal temperature gradient</td>
<td>2.11</td>
<td>5.0 $10^3$</td>
<td></td>
</tr>
</tbody>
</table>
3

KINETICS OF CO OXIDATION OVER Pt/γ-Al₂O₃

3.1 Introduction

The oxidation of CO by oxygen over group VIII metals has been studied extensively during the past decades. Individual processes essential to understanding the observed phenomena have gained much attention and there seems to be general consensus on most of the elementary steps comprising the reaction mechanism. Moreover, the use of modern computers allows simulation of the course of the individual processes from quantum chemistry (van Santen, 1991).


Oxygen adsorption was found to proceed dissociatively at temperatures above 100 K (Engel and Ertl, 1979, Luntz et al., 1989), however, molecularly adsorbed oxygen, referred to as physisorbed oxygen by Compton (1991), is often included in reaction mechanisms proposed for conditions at higher temperatures (Cant et al., 1978, Baddour et al., 1968). Additionally, taking into account molecular oxygen adsorption in elementary step kinetic modelling has been proven to be useful (Oh et al., 1986). This is substantiated physically by assuming molecular chemisorption of oxygen is followed by potentially faster dissociation (Boudart and Djéga-Mariadassou 1984). Significant associative desorption of oxygen has not been observed at temperatures lower than 700 K (Engel and Ertl, 1979, Luntz et al., 1989).

The CO₂ formation step is still debated: it is thought to proceed via a Langmuir-
Hinshelwood type surface reaction or through an Eley-Rideal reaction between either dissociatively chemisorbed oxygen and gas phase CO or, reversely, molecularly chemisorbed CO and gas phase O\textsubscript{2}. In literature a trend can be observed: before 1970 the Eley-Rideal mechanism predominated; publications by Bonzel and Ku (1973), Pacia \textit{et al.} (1976) and Golchet and White (1978), who explained their observations by both Langmuir-Hinshelwood and Eley-Rideal steps, changed this conviction. Since the work of Engel and Ertl (1978a, 1978b) and Campbell \textit{et al.}, (1980) the Langmuir-Hinshelwood mechanism prevails in literature. Moreover, in a theoretical study Weinberg has shown that under ultra-high vacuum conditions the rate of an Eley-Rideal reaction is negligible as compared to that of the Langmuir-Hinshelwood surface reaction. Under atmospheric conditions, however, no conclusive evidence has yet been published that rules out the Eley-Rideal reaction step.

High-vacuum results indicate the parameters of the elementary steps depend on the surface composition (Engel and Ertl, 1979, Herz and Marin, 1980, Bonzel and Ku, 1973, O’Rear \textit{et al.}, 1989, McCabe \textit{et al.}, 1988, Boudart and Rumpf, 1987). This implies a well known problem in interpreting kinetic data obtained under atmospheric pressure using supported catalysts (Compton, 1991): under these conditions the surface composition can hardly be determined, except to a certain extent by Positron Emission calculated Tomography (Vonkeman, 1990), so no direct evidence for occurrence of particular elementary steps can be obtained. CO oxidation by O\textsubscript{2} was found to proceed essentially via the same elementary steps over supported catalysts at atmospheric pressure as over single crystals under high-vacuum (Engel and Ertl, 1979, Boudart and Rumpf, 1987, Oh \textit{et al.}, 1986). For CO oxidation by NO over Rh this analogy between low and high pressure mechanisms does not seem to hold (Oh \textit{et al.}, 1986). This result suggests that kinetic parameters for CO oxidation by O\textsubscript{2} obtained under high-vacuum may be used as initial parameter estimates for modelling kinetic rate data obtained at atmospheric pressure.

Studies conducted at atmospheric pressure are a minority in the vast number of publications regarding CO oxidation. Berlowitz \textit{et al.} (1988). and Cant \textit{et al.} (1978) described the kinetics using empirical rate equations while Voltz \textit{et al.}, (1973) modelled the kinetics of CO oxidation in the presence of NO and C\textsubscript{3}H\textsubscript{8} using empirical reaction rate equations with adsorption terms, but without taking into account the reaction between CO and NO. Herz and Marin (1980) proposed a model using modified Langmuir-Hinshelwood mechanisms. Without kinetic parameter optimisation they were able to qualitatively simulate the rate data measured by Schlatter and Chou (1978). Subramaniam and Varma (1985) performed a kinetic study using CO, NO, O\textsubscript{2} and H\textsubscript{2}O. By kinetic parameter optimisation they fitted a kinetic model to their data, however, this model was not based on elementary reaction steps. Montreuil \textit{et al.}, (1992) carried out an extensive kinetic study using a full synthetic automotive exhaust and commercially available three-way catalysts, covering a wide range of reactant partial pressures at temperatures ranging from 640 to 900 K. Their model, however, is not based on elementary steps either.

The purpose of this study is to measure intrinsic kinetic production rates in a fixed-bed
reactor under a wide range of reactant partial pressures relevant to automotive exhaust catalyst at temperatures below light-off. In addition, the influence of steam on CO oxidation is assessed. The experimental data are used to estimate the value of the kinetic parameters of models based on elementary reaction steps by means of multiple non-linear regression analysis (Froment and Hosten, 1981). Regression analysis also allows model selection by identification of the model that best fits the rate data measured, provided the parameter estimates are physically feasible.

3.2 Experimental

Experiments described in this chapter have been carried out using a Pt/γ-Al₂O₃ catalyst prepared and pretreated as described in section 2.5. Depending on the type of experiment, CO oxidation either in the absence or in the presence of steam, catalysts were kept under flowing He or a He/H₂O mixture overnight at 473 K in order to prevent the catalyst from being contaminated.

**Effects potentially interfering with intrinsic kinetic measurements**

*Catalyst deactivation* was tested by regularly repeating an experiment carried out previously on the same catalyst batch. Since no significant differences in CO₂ production rates as a function of time on stream were measured the absence of deactivation was confirmed; the catalyst used maintained a stable activity for months. Catalyst batches only needed to be replaced if the preferred range of attainable $W/F_{CO,0}$ values required a different amount of catalyst.

In order to assess the existence of *hysteresis phenomena* often observed in experimental studies of CO oxidation by O₂ (Razon and Schmitz, 1986), each series of experiments was completed by repeating the first measurement of that series. No hysteresis occurred under the experimental conditions applied.

The maximum *axial temperature increase* measured amounted to 4 K at a reactor temperature of 503 K, in most experiments it was lower than 2 K. Therefore, the influence of axial temperature gradients on the net CO₂ production rate was considered negligible.

The influence of *heat and mass transport limitations* on the CO₂ production rate has been minimised by evaluating each CO₂ production rate measured, as illustrated in Chapter 2, Appendix II. In case at least one of the criteria was not met the observed CO₂ production rate was rejected. Under some circumstances these data could be acquired after all, for example by increasing the gas velocity in the reactor, resulting in better external heat and mass transfer.
Experimental conditions

Table 3.1

<table>
<thead>
<tr>
<th></th>
<th>absence of steam</th>
<th>presence of steam</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p$ / kPa</td>
<td>110</td>
<td>110</td>
</tr>
<tr>
<td>$P_{CO,0}$ / kPa</td>
<td>0.22 - 8.3</td>
<td>0.88 - 4.4</td>
</tr>
<tr>
<td>$P_{O_2,0}$ / kPa</td>
<td>0.37 - 8.3</td>
<td>0.44 - 4.4</td>
</tr>
<tr>
<td>$P_{CO_2}/P_{O_2,0}$ / -</td>
<td>0.1 - 3</td>
<td>0.33 - 7.7</td>
</tr>
<tr>
<td>$P_{H_2O}$ / kPa</td>
<td>0</td>
<td>0 - 10</td>
</tr>
<tr>
<td>$T^\circ$ / K</td>
<td>463 - 503</td>
<td>463 - 503</td>
</tr>
<tr>
<td>$W/F_{CO,0}$ / kg$_{soc}$ s mol$^{-1}$</td>
<td>8 - 60</td>
<td>8 - 60</td>
</tr>
<tr>
<td>$W$ / kg$_{soc}$</td>
<td>2.00 $10^{-3}$ / 6.00 $10^{-4}$</td>
<td>2.00 $10^{-4}$</td>
</tr>
</tbody>
</table>

The range of experimental conditions covered in this study is listed in Table 3.1. This range includes reactant partial pressures and temperatures encountered in realistic automotive exhaust catalysts. Within the boundaries of realistic process conditions the limits of the experimental conditions have been set according to two measures, the first being the requirements for measuring intrinsic kinetics (Chapter 2), the second being the sensitivity of the gas chromatograph towards CO$_2$. From introductory experiments it was found that the upper temperature limit allowing intrinsic kinetics to be measured under a range of reactant partial pressures amounted to 520 K; at higher temperatures up to approximately 900 K, which are beyond the scope of this study, the reaction rates are too high. At still higher temperatures the rates decrease due to a low CO surface coverage (Engel and Ertl, 1979), however, at those temperatures homogeneous gas phase reactions start to contribute significantly to CO$_2$ production (T’ien, 1981).

Experiments were carried out as follows. From the catalyst storage temperature of 483 K the catalyst was lined-out as described in the line-out section. Next, the reactor temperature was set to the desired value while the gas mixture was kept unchanged. Subsequently, the flow rates of the required components were set to the desired value in the sequence described in the line-out section; if necessary, the preheater temperature, see section 2.2, was adjusted so the temperature of the catalyst bed, as measured in the reactor axis immediately downstream of the catalyst bed entrance, was equal to the temperature of the outer reactor wall. Subsequently, after a minimum of 2 ks the molar flow rates of CO, O$_2$ and CO$_2$ were determined by GC analysis, this time being sufficiently long to reach a steady-state. All gas analyses were carried out in duplo; after setting new reaction conditions no gas analyses were performed within 2 ks. The gas analysis data were acquired as described in section 2.3 and processed according to the procedures in section 2.4.
Regression analysis

Regression of the experimental rate data to the proposed rate equations was performed by minimising the least squares criterion with respect to the observed and calculated CO$_2$ production rates. With $n$ observations and $p$ model parameters, the $p$-dimensional vector of maximum likelihood estimates $\hat{b}$ for the kinetic parameters $b$ is obtained by minimising $S(\hat{b})$ defined by:

$$S(\hat{b}) = \sum_{i=1}^{n} \left( R_{w,i} - \hat{R}_w(x_i, \hat{b}) \right)^2$$  (3.1)

where $R_{w,i}$ is the observed specific CO$_2$ production rate of observation $i$, and $\hat{R}_w(x_i, \hat{b})$ is the specific production rate calculated with parameter estimates $\hat{b}$, at the reaction conditions $x_i$ of observation $i$. The minimum value of $S(\hat{b})$ may be obtained by application of Eq. 3.2:

$$\frac{\partial S}{\partial \beta_j} \bigg|_{b_1 \ldots b_p} = 0$$  (3.2)

Minimisation was carried out using a single-response non-linear regression Marquardt algorithm (Froment and Hosten, 1981); 124 experiments, covering the complete range of experimental conditions listed in Table 3.1 were used in the regression, see Appendix III. Calculations were carried out using a DECStation 5000/100 Series workstation; typical CPU times for optimisation of one set of kinetic parameters ranged from seconds to thirty minutes, depending on the model regressed and the value of the initial parameter estimates.

The statistical significance of the individual parameter estimates was tested by their approximate $t$-values, based on the parameter value and its calculated standard deviation. With these $t$-values the $1-\alpha$ confidence intervals can be determined according to:

$$b_i - t(n-p, 1-\frac{1}{2}\alpha)s(b_i) \leq \hat{b}_i \leq b_i + t(n-p, 1-\frac{1}{2}\alpha)s(b_i)$$  (3.3)

The global statistical significance of the regression was assessed using the ratio of the mean regression sum of squares to the residual sum of squares, which is distributed according to $F$:

$$F - \text{ratio} = \frac{(n-p) \sum_{i=1}^{n} \hat{R}_{w,i}^2}{n \sum_{i=1}^{n} \left( R_{w,i} - \hat{R}_w(x_i, \hat{b}) \right)^2}$$  (3.4)

In order to avoid strong binary correlation between the Arrhenius parameters the Arrhenius equations were reparametrised according to (Kitrell, 1970):
CHAPTER 3

\[ k = A' \exp \left[ \frac{-E_a}{R} \left( \frac{1}{T} - \frac{1}{\bar{T}} \right) \right] \] (3.5)

where \( A' = A \exp \left[ \frac{-E_a}{RT} \right] \), and \( \bar{T} \) is the average temperature during the experiments, amounting to 483 K.

**Line-out procedure**

From introductory experiments it was found that the catalyst exhibited a higher initial activity after daily start-up as compared to the activity measured after more than five hours on stream. In order to minimise the influence of these reversible start-up effects on experimental results, a line-out procedure had to be carried out prior to kinetic measurements. The experimental conditions during the *in situ* line-out procedure are listed in Table 3.2. One minute after helium and, if applicable, steam flow rates were set CO was added to the reactor feed followed by \( \text{O}_2 \) after one minute. The reason for this sequence is that when \( \text{O}_2 \) was fed prior to CO, the catalyst bed sustained a transient temperature rise after adding CO, which caused a considerable delay in establishing steady-state. It was verified by carbon analysis that exposure to CO in the absence of oxygen at temperatures relevant to this study did not lead to significant coke deposition.

In Figure 3.1 the decay of \( R_w \) is shown versus time on stream after storage of the catalyst in flowing He. Since over 90% of the decay takes place in 10 ks kinetic experiments were carried out at least 10 ks after start-up; by comparing \( R_w \) to that measured after a previous line-out on the same catalyst batch the reproducibility of the experiments was ensured. Without steam in the

| Table 3.2  
Experimental conditions during catalyst line-out. |
<table>
<thead>
<tr>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Property</td>
</tr>
<tr>
<td>( p )</td>
</tr>
<tr>
<td>( p_{\text{CO},0} )</td>
</tr>
<tr>
<td>( p_{\text{CO}}/p_{\text{O}_2} )</td>
</tr>
<tr>
<td>( p_{\text{H}_2,0} )</td>
</tr>
<tr>
<td>( T )</td>
</tr>
<tr>
<td>( W/F_{\text{CO},0} )</td>
</tr>
</tbody>
</table>

**Figure 3.1**

\( \text{CO}_2 \) production rate in the absence of steam as a function of time on stream after catalyst storage in He at 473 K. Conditions: Table 3.2
overnight feed, realisation of a constant activity during experiments in the presence of steam required at least eight hours on stream after start-up. A similar procedure, keeping the catalyst under a reaction mixture for a certain period of time after pretreatment, prior to conducting kinetic experiments, has been reported by Vaporciyan et al. (1988) and Tenchev et al. (1992) for CO/O₂ experiments and by Pande and Bell (1986) for CO/NO experiments.

3.3 Influence of process variables on CO₂ production rate

Space time

All experiments in this study have been carried out under differential operating conditions. The influence of space time on the CO₂ production rate is then negligible, as has been shown in section 2.2. In Figure 3.2 the conversion of CO is plotted against the space time of CO, \( \frac{W}{F_{CO,0}} \), validating the assumption of differential reactor operation. \( X_{CO} \) is directly proportional to \( \frac{W}{F_{CO,0}} \) at least until \( X_{CO} \) equals 8%. As a result, in all experiments space time has been manipulated as to obtain CO conversions between 1% and 10%.

CO partial pressure

The net rate of production of CO₂ as a function of \( p_{CO} \) at three temperatures is shown in Figures 3.3 to 3.5. Qualitatively, the curves are similar for each temperature. At increasing CO partial pressure the CO₂ production rate decreases, indicating the reaction is inhibited by CO. An attempt was made to establish experimental conditions where the production of CO₂ was not inhibited by CO. Even at \( p_{CO}/p_{O₂} \) as low as 0.01 at a temperature of 483 K, \( R_w \) decreased with increasing \( p_{CO} \). This is in agreement with results published by Berlowitz et al. (1988), who
reported that CO inhibition plays an important role even at $p_{\text{CO}}/p_{\text{O}_2}|_0 = 0.005$ at temperatures lower than 700 K.

**Oxygen partial pressure**

Analogous to Figures 3.3 to 3.5 the effect of the oxygen partial pressure on the net rate of CO$_2$ production at temperatures of 463, 483 and 503 K, respectively, is represented by Figures 3.6 to 3.8. In all cases $R_w$ is essentially directly proportional to $p_{\text{O}_2}$. The implications of this result for the kinetic rate equation will be dealt with in detail in section 3.4. Increasing the CO partial pressure from 1.1 to 3.3 kPa results in a smaller slope of the $R_w$ versus $p_{\text{O}_2}$ curves, again indicating the reaction is inhibited by CO under the experimental conditions.
CO$_2$ partial pressure

To determine the net CO$_2$ production rate while CO$_2$ was fed to the reactor required calculation of $X_{CO}$ according to the direct method (Eq. 2.17) rather than using the normalisation method (Eq. 2.18), because $F_{CO,0}$ exceeded by far its extensive net production rate, i.e., the production rate in mol s$^{-1}$. Prior to feeding CO$_2$ it was verified that both methods yielded equal conversions under the experimental conditions considered.

In Figure 3.9 the influence of the CO$_2$ partial pressure on the net CO$_2$ production rate is shown. The presence of CO$_2$ does not significantly affect $R_w$ under the experimental conditions, which is in agreement with results published by Conrad et al. (1978), Campbell et al. (1980), and Solymosi (1991). Additionally, the variety of elementary steps proposed for CO oxidation over
platinum catalysts do not include CO$_2$ adsorption (Razon and Schmitz, 1986).

**Influence of steam**

Since automotive exhaust contains a considerable amount of steam, approximately 12 vol%, the influence of steam on the CO$_2$ production rate was measured under the experimental conditions listed in Table 3.1. Figure 3.10 shows the effect of the steam partial pressure on the net CO$_2$ production rate at fixed CO and O$_2$ partial pressures and a total pressure of 110 kPa. The presence of steam enhances the CO oxidation rate, the effect being most pronounced at low steam partial pressures. At steam partial pressures over 1 kPa the partial reaction order in $P_{H_2O}$ becomes zero. This could be due to a large adsorption equilibrium constant for dissociative adsorption of water on Al$_2$O$_3$, which, at low steam partial pressures, leads to saturation of the Al$_2$O$_3$ surface. No hydrogen could be detected in the reactor effluent, indicating the water-gas shift reaction does not occur significantly under the experimental conditions. Moreover, no other reaction products than CO$_2$ were observed, indicating no net disappearance of steam occurs.

Figure 3.11 shows the production rate of CO$_2$ as a function of the CO partial pressure in the presence and absence of steam. The presence of steam does not significantly influence the partial reaction order in $P_{CO}$, i.e. the rate enhancement by steam is not a function of $P_{CO}$.

Figure 3.12 shows the CO$_2$ production rate as a function of the oxygen partial pressure at three constant CO partial pressures and at three different temperatures. Again, the CO$_2$ production rate is enhanced by steam, the effect being more pronounced at lower temperatures, while the partial reaction order in the oxygen partial pressure is not affected. Since the rate enhancement

---

**Figure 3.10**

CO$_2$ production rate versus the steam partial pressure. Conditions: $P_{CO}$ = 0.88 kPa, $P_{O_2}$ = 2.2 kPa, $T$ = 483 K.

**Figure 3.11**

CO$_2$ production rate as a function of $P_{CO}$ in the absence and in the presence of steam. Conditions: $P_{O_2}$ = 2.2 kPa, $T$ = 483 K. +: $P_{H_2O}$ = 10 kPa, •: $P_{H_2O}$ = 0 kPa.
by steam is not influenced by $p_{CO}$, see Figure 3.11, it follows from Figure 3.12 that the rate enhancement by steam is a function of temperature.

**Figure 3.12**

$CO_2$ production rate as a function of $p_{O_2}$ in the absence and in the presence of steam.
Conditions: Left: $p_{CO}=1.1$ kPa, $T=463$ K; Centre: $p_{CO}=2.2$ kPa, $T=483$ K; Right: $p_{CO}=3.3$ kPa, $T=503$ K. +: $P_{H_2O}=10$ kPa, *: $P_{H_2O}=0$ kPa.

**Effect of temperature**

Figure 3.13 shows the temperature dependence of the $CO_2$ production rate in the absence and in the presence of steam. The apparent activation energies calculated from Figure 3.13 amount to 100 kJ mol$^{-1}$ both in the presence and in the absence of steam.

**3.4 Kinetic model development for CO oxidation**

As stated in the introduction of this Chapter, this study is aimed at elementary step kinetic modelling of CO oxidation, including the influence of steam on the oxidation kinetics. Figure 3.10 showed that CO oxidation was virtually zeroth order in the steam partial pressure. Since this implies that in this study the oxidation of CO
cannot be modelled using elementary reaction steps including water as a reactant, the kinetic
analysis in this section pertains to elementary step reaction paths for CO oxidation in the
absence of steam. Subsequently, the influence of steam will be evaluated using the kinetic
model as selected after regression analysis of the rate data measured in the absence of steam.

In all kinetic models derived in this section the steady-state approximation has been
applied. Furthermore, kinetic rate equations have been set up in accordance with the

Elementary reaction steps

In order to understand and quantify the experimental observations, several reaction
paths, leading to the same global reaction of CO oxidation can be proposed. The reaction
paths considered and the corresponding elementary steps are listed in Table 3.3, where the
stoichiometric numbers \( \sigma \) of the reactions express the number of times each reaction has to
proceed for the corresponding closed sequence to turn-over once. Each reaction path consists
of a closed sequence of elementary steps, the choice of elementary steps from the variety of
steps reported in literature being based on the observed dependencies of \( R_w \) on the process
conditions. In step (2) the backward reaction, associative desorption of oxygen, has been
omitted since no significant associative desorption of oxygen has been reported for the process
conditions applied in this study. Steps (3-1), (3-2) and (4) have been adopted as to allow for
the direct proportionality between the rate of oxygen adsorption and the fraction of vacant
active sites (Oh et al., 1986), despite the fact that molecularly adsorbed oxygen has not been
identified under the experimental conditions. Except for the reaction steps describing
molecular chemisorption of \( \text{O}_2 \) followed by its dissociation, these elementary steps are among
the most frequently reported (Razon and Schmitz, 1986, Harold and Garske, 1991a, 1991b,

Based on the reaction paths \( A \) to \( F \) in Table 3.3 six kinetic rate expressions can be
derived, expressing the specific production rate of \( \text{CO}_2 \) as a function of the process conditions.
Since these rate expressions may be complex due to the non-linearity of the kinetics, it is
convenient to apply a simplifying assumption: the existence of a rate-determining step.

Assuming the existence of a rate-determining step in CO oxidation over Pt catalysts is
rather awkward, since the formal definition of a rate-determining step requires that all steps
but the one denoted rate determining are at quasi-equilibrium and that the rate-determining
step is a two-way\(^1\) step. If more than one step has non-zero affinity, this definition cannot
be strictly applied. However, Boudart and Tamaru (1991) provided an operational definition

\(^1\)Following the terminology of Boudart and Tamaru (1991) a reaction is said to go one-way if the rate of
the reverse reaction is negligibly small. The terms one-way and two-way are used rather than 'irreversible' and
'reversible' as to discriminate between kinetics and thermodynamics.
**Table 3.3:**
Elementary step reaction paths considered in kinetic modelling of CO oxidation by O\(_2\) in the absence of steam.
Each reaction path A to F consists of \(\{\sigma_{\text{step } i}, ..., \sigma_{\text{step } 6}\}\) where \(\sigma_{\text{step } i}\) is the stoichiometric number for step \(i\).

<table>
<thead>
<tr>
<th>Elementary step</th>
<th>Reaction path</th>
<th>(\sigma_A)</th>
<th>(\sigma_B)</th>
<th>(\sigma_C)</th>
<th>(\sigma_D)</th>
<th>(\sigma_E)</th>
<th>(\sigma_F)</th>
<th>step number</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO + *</td>
<td>(k_f^i) (\equiv) CO*</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>(1)</td>
</tr>
<tr>
<td>(k_i^b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O(_2) + 2*</td>
<td>(k_f^2) (\rightarrow) 2O*</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>(2)</td>
</tr>
<tr>
<td>O(_2) + *</td>
<td>(k_f^3) (\equiv) O(_2)*</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>(3-1)</td>
</tr>
<tr>
<td>O(_2) + *</td>
<td>(k_f^4) (\equiv) O(_2)*</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>(3-2)</td>
</tr>
<tr>
<td>O(_2)* + *</td>
<td>(k_f^5) (\equiv) 2O*</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>(4)</td>
</tr>
<tr>
<td>CO + O*</td>
<td>(k_{LR}) (\rightarrow) CO(_2) + 2*</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>(5)</td>
</tr>
<tr>
<td>CO + O*</td>
<td>(k_{ER}) (\rightarrow) CO(_2) + *</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>(6)</td>
</tr>
<tr>
<td>2CO + O(_2)</td>
<td>(\rightarrow) 2CO(_2)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

for the rate-determining step if either a one-way reaction is rate determining or more than one steps are not at quasi-equilibrium. Their definition states that for a one-way catalytic cycle the rate-determining step is the one-way step whose forward rate coefficient is the only one to appear in the rate equation for the overall one-way reaction. This definition is equivalent to stating that the rate-determining step is the only kinetically significant step that is not at quasi-equilibrium. Clearly, this definition is useful, because it allows extracting kinetic information from simplified models that would otherwise be obscured by kinetically insignificant parameters.

A second simplifying assumption can be made: adoption of the *most abundant reaction intermediate* concept (Boudart and Djéga-Mariadassou, 1984). Application of this concept in CO oxidation is supported by the fact that under conditions typical for studies at higher pressure the surface coverage of CO is far superior to the coverages of the other surface species (Engel and Ertl, 1979, Berlowitz *et al.*, 1988), so the latter may be left out of the active site balance. The reaction paths in Table 3.3 will now be submitted to a kinetic
analysis; reaction step numbers in the discussion refer to the elementary steps from Table 3.3.

**Reaction path A**

In reaction path A from Table 3.3 dissociative oxygen adsorption is thought to proceed in one step, while the surface reaction takes place via a Langmuir-Hinshelwood reaction. Assuming mass action kinetics, the surface coverages may be solved from the continuity equation for the surface species, Eqs. 3.6 to 3.8.

\[
k_1^f p_{CO} \theta_* - k_1^b \theta_{CO} - k_{LH} \theta_{CO} \theta_O = 0 \quad (3.6)
\]

\[
2k_2^f p_{O2} \theta_*^2 - k_{LH} \theta_{CO} \theta_O = 0 \quad (3.7)
\]

\[
\theta_{CO} + \theta_O + \theta_* = 1 \quad (3.8)
\]

Subsequently, the solutions for \( \theta_{CO} \) and \( \theta_O \) are substituted in the rate equation:

\[
\dot{R}_w = k_{LH} \theta_{CO} \theta_O L_t \quad (3.9)
\]

where \( L_t \) denotes the specific concentration of active sites, *i.e.* in units of mol kg\(_c\)\(^{-1}\). This procedure leads to a multitude of complex rate equations, so simplification is necessary. The first simplification is the assumption of CO adsorption equilibrium, leading to the kinetic rate expression Eq. 3.10.

\[
\dot{R}_w = \frac{2k_2^f p_{O2} \theta_*^2}{k_{LH} K_1^f k_2^f p_{CO} p_{O2} L_t} \quad (3.10)
\]

If, in addition, oxygen adsorption is assumed to be rate determining, implying \( \theta_O \ll \theta_* \) and \( \theta_O \ll \theta_{CO} \), the rate expression Eq. 3.11 is obtained.

\[
\dot{R}_w = 2 \frac{k_2^f p_{O2} L_t}{(1 + K_1 p_{CO})^2} \quad (3.11)
\]

If \( \theta_{CO} \gg \theta_* \), Eq. 3.11 reduces to:

\[
\dot{R}_w = 2 \frac{k_2^f p_{O2} L_t}{K_1^2 p_{CO}} \quad (3.12)
\]
Reaction path B

Reaction path B differs from path A with respect to the surface reaction step, which in path B is represented by an Eley-Rideal reaction between adsorbed oxygen and gas-phase CO. Note that in this model adsorbed CO does not take part in the formation of CO₂, hence, the establishment of adsorption equilibrium for CO is evident. On solving the continuity equations for the surface species, cf. Eqs. 3.6 to 3.8, two solutions are obtained for θ₀, which after substitution in the rate equation, Eq. 3.13, leads to Eq. 3.14.

\[
\dot{R}_w = k_{ER} \theta_O P_{CO} L_t
\]  

(3.13)

\[
\dot{R}_w = \pm \left[ \sqrt{k_{ER} k_1^2 P_{CO}^2} + 2k_{ER} K_1 P_{CO} + 8k_2 k_{CO} P_{O_2} - k_{ER} K_1 P_{CO} - k_{ER} P_{CO} \right] L_t^2 /

(3.14)

Assuming oxygen adsorption is rate determining followed by the assumption that CO* is the most abundant reaction intermediate leads to the same rate equations that were derived for reaction path A, Eq. 3.11 and Eq. 3.12, respectively. This is obvious, since paths A and B only differ as far as the surface reaction step is concerned; by the simplifying assumptions the reaction step is rendered kinetically insignificant. This indicates that no discrimination between a Langmuir-Hinshelwood step and an Eley-Rideal step can be made on the basis of the simplified models from reaction paths A and B.

Reaction path C

In reaction path C oxygen adsorption is thought to proceed in two steps in series, first one-way molecular chemisorption of O₂ followed by dissociation of O₂*, steps (3-1) and (4) in Table 3.3. CO₂ formation takes place via a Langmuir-Hinshelwood surface reaction. Substitution of the solutions of the continuity equations for the surface species into Eq. 3.9, leads to the rate expression:

\[
\dot{R}_w = \frac{2k_1^b k_3^f k_4^f}{k_{\text{LH}} k_4^b} \left[ k_{\text{LH}} k_4^b P_{CO} - k_{\text{LH}} k_4^f P_{CO} P_{O_2} - 2k_1^b k_4^f P_{O_2} + 2k_3^f k_{\text{LH}} P_{O_2} - 2k_{\text{LH}} k_4^f k_3^f P_{O_2} \right] L_t /

k_{\text{LH}} k_4^b \left[ k_{\text{LH}}^b P_{CO} + k_1^f - 2k_3^f P_{O_2} \right] \left( k_{\text{LH}}^f P_{CO} - 2k_3^f P_{O_2} \right)
\]  

(3.15)

Assuming CO adsorption equilibrium leads to:
\[ \dot{R}_w = \frac{2k_3^f p_{O_2} \left( k_{LH} K_1 k_4 p_{CO} - 2 k_3^f k_4 p_{O_2} - k_{LH} K_1 k_3^f p_{CO} p_{O_2} \right) L_t}{k_{LH} k_4 K_1 p_{CO} \left( 1 + K_1 p_{CO} \right)} \]

(3.16)

If O\(_2\) chemisorption, step (3-1), is considered rate determining, implying \( \theta_{O_2} < \theta_o < \theta_s \), the rate expression is simplified to:

\[ \dot{R}_w = \frac{2k_3^f p_{O_2} L_t}{1 + K_1 p_{CO}} \]

(3.17)

and, with CO\(^*\) as the most abundant reaction intermediate Eq. 3.18 is obtained.

\[ \dot{R}_w = \frac{2k_3^f p_{O_2} L_t}{K_1 p_{CO}} \]

(3.18)

**Reaction path D**

In path D oxygen chemisorption and dissociation proceed similarly to path C; the reaction takes place via the Eley-Rideal step, step (6) in Table 3.3, and because adsorbed CO does not take part in the reaction, CO adsorption equilibrium is established. Eq. 3.19 is obtained as expression for the specific CO\(_2\) production rate.

\[ \dot{R}_w = \frac{2k_{ER} k_3^f p_{CO} p_{O_2} \left[ 1 - \frac{k_3^f}{k_4} p_{O_2} \right] L_t}{2k_3^f p_{O_2} + k_{ER} K_1 p_{CO}^2 + k_{ER} p_{CO}} \]

(3.19)

Assuming that molecular chemisorption of oxygen is rate determining and, additionally, that CO\(^*\) is the most abundant reaction intermediate leads to the same rate expressions that were found for reaction path C, Equations 3.17 and 3.18. Again, this is due to the fact that the reaction step is not kinetically significant, so no discrimination between a Langmuir-Hinshelwood or an Eley-Rideal reaction is possible.

The most important phenomenological difference between the simplified rate equation for reaction paths C and D, Eq. 3.18, and that of reaction paths A and B, Eq. 3.12, is that in the former paths the CO\(_2\) production rate is inversely proportional to \( p_{CO}^2 \), while in the latter this rate is inversely proportional to \( p_{CO} \).
Reaction paths $E$ and $F$

Reaction paths $E$ and $F$ correspond to paths $C$ and $D$, respectively, the difference being that now desorption of molecularly chemisorbed oxygen is taken into account. Again, simplification is necessary in order to obtain functional rate expressions, if adsorption equilibrium is assumed for CO and O$_2$, the rate expression resulting for path $E$ is:

$$
\dot{R}_w = \frac{2k_L^2K_1^2k_4K_3p_{CO}p_{O_2}L_t}{\left(2k_4K_3p_{O_2} + k_LK_1^2p_{CO} + k_LK_1K_3p_{CO}p_{O_2} + k_LK_1p_{CO}\right)^2}
$$

(3.20)

If dissociation of O$_2^*$, step (4) in Table 3.3, is considered rate determining in reaction path $E$, implying $\theta_O < \theta_e$, $\theta_O < \theta_{O_2}$ and $\theta_O < \theta_{CO}$, Eq. 3.20 is reduced to:

$$
\dot{R}_w = \frac{2k_4K_3p_{O_2}L_t}{\left(1 + K_1p_{CO} + K_3p_{O_2}\right)^2}
$$

(3.21)

Both assumptions made for path $E$ do not result in practical rate expressions for path $F$. Assuming CO$^*$ is the most abundant reaction intermediate leads to Eq. 3.22 for both reaction paths $E$ and $F$.

$$
\dot{R}_w = \frac{2k_4K_3p_{O_2}L_t}{K_1^2p_{CO}^2}
$$

(3.22)

3.5 A priori values of kinetic parameters

The kinetic parameters appearing in the rate expressions presented in section 3.4 may be estimated from collision theory and transition state theory. If elementary steps are described in an Arrhenius form then pre-exponential factors can be estimated from spectrometrically accessible quantities, e.g., vibrational frequencies of adsorbed species. Pre-exponential factors based on theoretical considerations are often presented as ranges of feasible values. For that reason values adopted in this section serve as initial parameter estimates for kinetic modelling purposes, rather than being accurate predictions. First the rate coefficients used in the kinetic models will be addressed, followed by a table of initial estimates for the parameters included in the rate coefficients, Table 3.4.

Chemisorption

From collision theory the rate coefficient of chemisorption in units of mol$\_f$ mol$\_pt$ $^{-1}$ Pa$^{-1}$ s$^{-1}$ is expressed as:
Often, the initial sticking probability is described by (Engel and Ertl, 1979, Herz and Marin, 1980, Boudart and Djéga-Mariadassou, 1984):

$$s_0 = s_0^0 f(0) \exp \left( \frac{-E_{a,ads}}{RT} \right)$$  \hspace{1cm} (3.24)

where $s_0^0$ refers to the initial sticking probability at a reference temperature.

In the models presented in section 3.4 the dependence of the sticking probability on the surface coverage has been expressed explicitly by including $\theta_s$ in the chemisorption rate equations, according to the Langmuir-Hinshelwood-Hougen-Watson formalism. Molecular chemisorption of CO and O$_2$ have been reported to be essentially non-activated processes (Engel and Ertl, 1978b, Palmer and Smith, 1974 and Bonzel and Ku, 1973, Boudart and Rumpf, 1987, respectively). For dissociative chemisorption Herz and Marin (1980), assume a small negative activation energy amounting to -4.2 kJ mol$^{-1}$.

Desorption

The desorption coefficient can be described by:

$$k_{des} = A_{des} \exp \left( \frac{-E_{a,des}}{RT} \right)$$  \hspace{1cm} (3.25)

in which $E_{a,des} \approx -\Delta H_{ads}^{0}$ if adsorption is non-activated. The turnover frequency for CO desorption is often described as (Engel and Ertl, 1979, Herz and Marin, 1980, Boudart and Djéga-Mariadassou, 1984):

$$N_{des}^{CO} = A_0 \exp \left( \frac{-E_{a,des}^{CO}(0)}{RT} \right) \theta_{CO}$$  \hspace{1cm} (3.26)

The relationship between the turnover frequency $N$ and the specific production rate $R$ has been mentioned in Eq. 2.21.

Herz and Marin (1980), Oh et al. (1986) and Sant and Wolf (1990) express a linear surface coverage dependence of $E_a$ as Elovich desorption kinetics (Boudart and Djéga-Mariadassou, 1984):

$$E_{a,des}^{CO} = E_{a,des}^{CO,0} - \alpha \theta_{CO}$$  \hspace{1cm} (3.27)
In Eq. 3.27 the factor $\alpha$ accounts for the interaction of adsorbed CO molecules. This indicates a deviation from the Langmuir hypothesis expressing that all active sites are thermodynamically and kinetically equal. Since the experimental results presented in section 3.3 indicate a high $\theta_{CO}$ under the experimental conditions this explicit dependence of $E_{a,des}$ on $\theta$ has not been adopted.

**Surface Reaction**

The rate coefficient for the Langmuir-Hinshelwood step is described by:

$$k_{LH} = A_r^{LH} \exp \left( \frac{-E_{a,r}^{LH}}{RT} \right)$$  \hspace{1cm} (3.28)

For the Eley-Rideal step the rate coefficient is calculated according to:

$$k_{ER} = A_r^{ER} \exp \left( \frac{-E_{a,r}^{ER}}{RT} \right)$$  \hspace{1cm} (3.29)

In Table 3.4 the quantities required for estimating the Arrhenius parameters of the kinetic models are listed.

### 3.6 Kinetic model selection and discussion

**Model selection**

The main result of the regression analysis is that, under the wide range of experimental conditions applied in this study, the assumptions of CO adsorption equilibrium and of CO* being the most abundant reaction intermediate are valid. As a result, all experiments in this study have been carried out at CO coverages close to unity. Regression using models without these assumptions did not result in statistically significant parameter estimates. This indicates that under conditions relevant to automotive catalysts at temperatures well below light-off, steady state CO oxidation by $O_2$ can be described using fairly simple algebraic rate expressions such as:

$$\dot{R}_w = A^{global} \exp \left( \frac{-E^{global}_a}{RT} \right) f(p_{CO}, p_{O_2}) L_1$$  \hspace{1cm} (3.30)

in which $f(p_{CO}, p_{O_2})$ is described by Eq. 3.31 for reaction paths $A$, $B$, $E$ and $F$:
### Table 3.4

**A priori values of the kinetic parameters allowing calculation of turnover frequencies. Calculation of \( R_w \) according to Eq. 2.21**

<table>
<thead>
<tr>
<th>quantity</th>
<th>value</th>
<th>dimension</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( s_{0,CO} )</td>
<td>0.5</td>
<td>--</td>
<td>Herz and Marin, 1980</td>
</tr>
<tr>
<td>( s_{0,O_2} )</td>
<td>0.012</td>
<td>--</td>
<td>Herz and Marin, 1980</td>
</tr>
<tr>
<td>( \sigma )</td>
<td>( 4 \times 10^4 )</td>
<td>m² mol⁻¹</td>
<td>Herz and Marin, 1980</td>
</tr>
<tr>
<td>( A_{des}^{CO} )</td>
<td>( 10^{14}, 10^{12}, 10^{13} )</td>
<td>s⁻¹</td>
<td>van Santen and Niemantsverdriet, 1992; Zhdanov et al., 1988; Compton, 1991</td>
</tr>
<tr>
<td>( E_{CO}^{des} )</td>
<td>( 145 \times 10^3, 130 \times 10^3 )</td>
<td>J mol⁻¹</td>
<td>Campbell et al., 1980; Herz and Marin, 1980; Compton, 1991</td>
</tr>
<tr>
<td>( A_{ad}^{CO} )</td>
<td>( 10^1 )</td>
<td>Pa⁻¹ s⁻¹</td>
<td>Zhdanov et al., 1988</td>
</tr>
<tr>
<td>( E_{ad}^{CO} )</td>
<td>0</td>
<td>J mol⁻¹</td>
<td>Compton, 1991</td>
</tr>
<tr>
<td>( \Delta H_{ad}^{O_2} )</td>
<td>( -130 \times 10^3 )</td>
<td>J mol⁻¹</td>
<td>Compton, 1991 (( E_{ad}^{ads} - E_{ad}^{des} ))</td>
</tr>
<tr>
<td>( A_{ads}^{O_2} )</td>
<td>( 10^5 )</td>
<td>Pa⁻¹ s⁻¹</td>
<td>Zhdanov et al., 1988</td>
</tr>
<tr>
<td>( E_{a,dis}^{O_2} )</td>
<td>( 10 \times 10^3 ), 0</td>
<td>J mol⁻¹</td>
<td>Campbell et al., 1991; Zhdanov et al., 1988</td>
</tr>
<tr>
<td>( A_{des}^{O_2} )</td>
<td>( 6.5 \times 10^7 )</td>
<td>s⁻¹</td>
<td>Wilf and Dawson, 1977</td>
</tr>
<tr>
<td>( E_{a,des}^{O_2} )</td>
<td>( 210 \times 10^3, 130 \times 10^3 )</td>
<td>J mol⁻¹</td>
<td>Compton, 1991; Wilf and Dawson, 1977</td>
</tr>
<tr>
<td>( \Delta H_{ads}^{O_2} )</td>
<td>( -210 \times 10^3 )</td>
<td>J mol⁻¹</td>
<td>Compton, 1991 (( E_{ads}^{ads} - E_{ads}^{des} ))</td>
</tr>
<tr>
<td>( A_{ads}^{O_2} )</td>
<td>( 10^{12} )</td>
<td>Pa⁻¹ s⁻¹</td>
<td>Luntz et al., 1989</td>
</tr>
<tr>
<td>( E_{a,ads}^{O_2} )</td>
<td>( 10 \times 10^3 )</td>
<td>J mol⁻¹</td>
<td>Luntz et al., 1989</td>
</tr>
<tr>
<td>( A_{des}^{O_2} )</td>
<td>( 1.7 \times 10^9 )</td>
<td>s⁻¹</td>
<td>Wilf and Dawson, 1977</td>
</tr>
<tr>
<td>( E_{a,des}^{O_2} )</td>
<td>( 130 \times 10^3 )</td>
<td>J mol⁻¹</td>
<td>Wilf and Dawson, 1977</td>
</tr>
<tr>
<td>( \Delta H_{ads}^{O_2} )</td>
<td>( -120 \times 10^3 )</td>
<td>J mol⁻¹</td>
<td>(( E_{ads}^{ads} - E_{ads}^{des} ))</td>
</tr>
<tr>
<td>( A_{ads}^{O_2} )</td>
<td>( 8 \times 10^7 )</td>
<td>s⁻¹</td>
<td>Luntz et al., 1989 &amp; Wilf and Dawson, 1977</td>
</tr>
<tr>
<td>( E_{a,dis}^{O_2} )</td>
<td>( 125 \times 10^3 )</td>
<td>J mol⁻¹</td>
<td>Luntz et al., 1989 &amp; Wilf and Dawson, 1977</td>
</tr>
<tr>
<td>( A_r^{LH} )</td>
<td>( 10^{13}, 2 \times 10^{14} )</td>
<td>s⁻¹</td>
<td>Herz and Marin, 1980; Campbell et al., 1980</td>
</tr>
<tr>
<td>( E_{a,r}^{LH} )</td>
<td>( 56 \times 10^3, 110 \times 10^3, 100 \times 10^3 )</td>
<td>J mol⁻¹</td>
<td>Herz and Marin, 1980; Weinberg and Merrill, 1975; Campbell et al., 1980</td>
</tr>
<tr>
<td>( A_r^{ER} )</td>
<td>( 10^1, 3 \times 10^2 )</td>
<td>Pa⁻¹ s⁻¹</td>
<td>Zhdanov et al., 1988; Pacia et al., 1976</td>
</tr>
<tr>
<td>( E_{a,r}^{ER} )</td>
<td>( 70 \times 10^3, 0 )</td>
<td>J mol⁻¹</td>
<td>Weinberg and Merrill, 1975; Pacia et al., 1976</td>
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**Key:**
- \(^a\) Highest value reported;
- \(^b\) Parameters for second order \( O_2 \) desorption;
- \(^c\) Parameters for \( O_2 \) chemisorption from physisorbed state;
- \(^d\) Parameters for first order \( O_2 \) desorption;
- \(^e\) Calculated from \( A_{ads}^{O_2}/A_{dis}^{O_2} = 20 \) (Luntz et al., 1989);
- \(^f\) Calculated from \( E_{a,des}^{O_2} - E_{a,dis}^{O_2} = 5 \) kJ mol⁻¹ (Luntz et al., 1989).

If more values are listed the last one has been used in the estimates. Data taken from Compton, 1991, refer to polycrystalline Pt.
\[ f(p_{CO}, p_{O_2}) = \frac{p_{O_2}}{p_{CO}} \]

(3.31)

and by Eq 3.32 for reaction paths C and D:

\[ f(p_{CO}, p_{O_2}) = \frac{p_{O_2}}{p_{CO}} \]

(3.32)

In the parameters \( a^{\text{global}} \) and \( E_a^{\text{global}} \) in Eq. 3.30 the pre-exponential factors and temperature dependencies of the individual processes are lumped, indicating that the physical interpretation of these parameters depends on the model considered. The physical interpretation of the global pre-exponential factor and global activation energy and their estimates with their 95% confidence intervals are shown in Table 3.5.

Considering the \( F \)-values, rate equation 3.18 describes the experimental results more adequately than the other models. Rate equation 3.18 corresponds to reaction paths C and D, where molecular adsorption of oxygen is considered rate determining, and CO is the most abundant reaction intermediate. This indicates that under the experimental conditions molecular adsorption of oxygen rather than the commonly expected (Oh et al., 1986) direct dissociative chemisorption is the rate-determining step. Another indication for molecular adsorption of oxygen as rate-determining step is found if the physical significance of the kinetic parameters is assessed.

The global activation energy estimated for Eq. 3.18 is in good agreement with the experimental value calculated from Figure 3.13, whereas the activation energies estimated for rate equations 3.12 and 3.22 are approximately twice as large as the value determined experimentally. In the rate equation 3.18 the activation energy consists of the CO adsorption enthalpy and the activation energy for oxygen chemisorption. Since chemisorption is essentially non-activated, see section 3.5, the former equals \(-\Delta H_{\text{des}}^{\text{CO}}\), while the latter is close to zero. The value estimated using Eq. 3.18 is lower than \(\Delta H_{\text{des}}^{\text{CO}}\) on an empty Pt surface, which is approximately 125 kJ mol\(^{-1}\) (Herz and Marin, 1980). However, as discussed in section 3.5, a surface coverage dependence is often included in CO desorption, see Eqs. 3.26 and 3.27. In Eq. 3.27 the factor \( \alpha \) accounts for the interaction of adsorbed CO molecules; \( \alpha \) amounts to 27.2 kJ mol\(^{-1}\) (Herz and Marin, 1980), which leads to an activation energy of desorption of 97 kJ mol\(^{-1}\) for \( \theta_{\text{CO}} \) sufficiently close to unity. The value of \( E_a^{\text{app}} \) estimated using Eq. 3.18 is in agreement with this value.

This result, model selection aided by the physical validity of the kinetic parameter estimates, is very important because it confirms the outcome of the mathematical treatment of elementary steps. Without assessing the physical validity of kinetic parameter estimates the application of regression analysis might be debatable.
Table 3.5
Physical interpretation and estimates of the global pre-exponential factors and global activation energies with their 95% confidence intervals obtained by regression of the data acquired in the absence of steam with rate equations 3.12, 3.18 and 3.22

<table>
<thead>
<tr>
<th>Rate equation</th>
<th>Physical interpretation of the global parameters</th>
<th>Initial value calculated from Table 3.4</th>
<th>value after regression</th>
<th>$F^*$ value</th>
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<td>$A_{\text{global}} = 2k_2 \left( \frac{k_f}{A_{\text{des}}} \right)^{-2}$</td>
<td>/Pa s$^{-1}$</td>
<td>2.0 $10^{29}$</td>
<td>(6.68 ± 1.32) $10^{30}$</td>
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<td>$E_a^{\text{global}} = -2\Delta H_{\text{ads}}^{\text{CO}}$</td>
<td>/kJ mol$^{-1}$</td>
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<td>275.5 ± 22.7</td>
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<td>$A_{\text{global}} = 2k_3 \left( \frac{k_f}{A_{\text{CO}}} \right)^{-1}$</td>
<td>/s$^{-1}$</td>
<td>5.7 $10^{11}$</td>
<td>(5.40 ± 0.35) $10^{11}$</td>
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<td>$E_a^{\text{global}} = -\Delta H_{\text{ads}}^{\text{CO}} + E_{\text{ads}}^{\text{O}_2}$</td>
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<td>112.1 ± 7.8</td>
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<td>$A_{\text{global}} = 2A_{\text{ads}}^{\text{O}<em>2} \frac{A</em>{\text{ads}}^{\text{O}<em>2}}{A</em>{\text{des}}^{\text{O}<em>2}} \left( \frac{k_f}{A</em>{\text{des}}} \right)^{-2}$</td>
<td>/Pa s$^{-1}$</td>
<td>1.9 $10^{31}$</td>
<td>(6.68 ± 1.32) $10^{30}$</td>
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<tr>
<td>$E_a^{\text{global}} = E_{\text{ads}}^{\text{O}<em>2} + \Delta H</em>{\text{ads}}^{\text{O}<em>2} - 2\Delta H</em>{\text{ads}}^{\text{CO}}$</td>
<td>/kJ mol$^{-1}$</td>
<td>255</td>
<td>275.5 ± 22.7</td>
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As stated before, no discrimination can be made between a Langmuir-Hinshelwood or an Eley Rideal reaction, because under the experimental conditions these steps are kinetically insignificant. The results of the kinetic modelling of CO oxidation in the absence of steam are summarised in Figure 3.14, in which the CO$_2$ production rates calculated using Eq. 3.18, are shown as a function of the measured values.

Figures 3.15 and 3.16 illustrate the quality of the model description of the experimental data. Figure 3.15 shows the measured and calculated production rates of CO$_2$ as a function of $p_{\text{CO}}$ at three oxygen partial pressures at 483 K. Figure 3.16 shows $R_w$ as a function of $p_{\text{O}_2}$.
The CO₂ production rate as function of $p_{CO}$ is appropriately simulated whereas the dependence of $R_w$ on $p_{O2}$ is simulated significantly worse at lower oxygen partial pressures; the experimental production rates are higher than those predicted by the model, the difference increasing with increasing $p_{CO}$. It should be emphasised that the discrepancy between measured and calculated CO₂ production rates at low oxygen partial pressures is not caused by an experimental artefact.

In order to explain the observed divergence between calculated and measured CO₂ production rates a number of possible explanations can be proposed. The most straightforward explanation is that, although γ-Al₂O₃ was found to be essentially inert under reaction conditions, it may influence the reaction in the presence of platinum by inverse spill-over of oxygen. Considering the fact that the fraction of the Al₂O₃ surface covered by platinum is smaller than 1%, it is clear that even a rather small areal adsorption rate of oxygen on Al₂O₃ may result in considerable amounts of adsorbed oxygen species relative to the amount of oxygen adsorbed on platinum. In combination with the fact that at low oxygen partial pressures the conversion of CO was low, this may explain a relatively large contribution to the global CO₂ production rate of oxygen supply via the support, provided inverse spill-over of oxygen is sufficiently fast.

Another, yet still debated, possible explanation is surface reconstruction and its influence on the turnover frequency (Figueras et al., 1980). From a comparison of kinetic data obtained with Pt, Ir and Pd single crystals under UHV-conditions and data from studies using polycrystalline and supported platinum catalysts, Berlowitz (1988) concluded that the reaction was structure insensitive. Ertl (1990), however, concluded the reaction is structure sensitive if the surface is mainly covered with CO*, that is, when the rate
is limited by oxygen adsorption, because the sticking probability of oxygen is structure sensitive. It has been reported that Pt surface reconstructions occur depending on the gas atmosphere, e.g., on exposure to CO the fraction of stepped sites increases (Somorjai, 1980). Hopster et al. (1977) reported an increased sticking probability for oxygen on increasing the abundance of these stepped sites. Since oxygen adatoms were bonded more strongly to these sites, this did not yield an increased CO₂ production rate under the operating conditions in their study. Since in the present study oxygen chemisorption was found to be rate determining, an increased sticking probability would lead to a higher CO₂ production rate. However, it is not fully understood which surfaces do or do not reconstruct under certain conditions (Somorjai, 1980).

Influence of steam on kinetic parameter estimates

In the previous section it was stated hypothetically that the influence of steam on the CO oxidation kinetics could be expressed using the kinetic model valid in the absence of steam. This hypothesis was tested by regressing the experimental rate data acquired in the presence of steam, under the experimental conditions listed in Table 3.1, using the simplified rate expression Eq. 3.18. Modelling was carried out according to the method described in section 3.2. The maximum likelihood parameter estimates calculated for the reaction in the absence of steam, shown in Table 3.5, were taken as initial kinetic parameter estimates.

The resulting maximum likelihood parameter estimates and their statistical relevance are shown in Table 3.6. The t-values show the estimates are statistically significant while the F-value indicates a statistically significant global fit. The corresponding parity diagram of calculated CO₂ production rates using rate equation 3.18 versus the experimental rate data is shown in Figure 3.17; a comparison between experiments and simulations is shown in Figures 3.18 and 3.19.

The observed rate enhancement by steam is in agreement with results published by Hegedus et al. (1977), Chakrabarty et al. (1984) and Muraki et al. (1991). These authors do not

![Graph](image)

**Table 3.6**

Maximum likelihood estimates for the global pre-exponential factor and the global activation energy with their 95% confidence interval obtained by regression of the data acquired in the presence of steam, see Appendix III with rate equation 3.18.
assign the observed rate enhancement to the occurrence of water-gas shift, either, since the reaction temperatures were below 600 K. Instead, Hegedus et al. (1977) and Muraki et al. (1991) proposed that the presence of steam affects the CO oxidation equilibrium, resulting in decreased CO inhibition and, consequently, higher rates. This is in disagreement with the observed CO₂ production rates measured in the presence and in the absence of steam at a temperature of 503 K, see Figure 3.12. The rate enhancement by steam is moderate at that temperature, while the experiments were carried out within the limits of the CO inhibition regime. Hence, following Hegedus et al. (1977) and Muraki et al. (1991), a clear rate enhancement should have been observed.

The estimated value of the global activation energy is 20 % lower than the one in the absence of steam. This decrease in global activation energy is not likely to be caused by repulsive interaction of CO and OH-groups on the platinum surface because, under the experimental conditions, water does not adsorb significantly on the Pt surface (Heras and Viscido, 1988). Water does, however, adsorb both molecularly and dissociatively on Al₂O₃ forming hydroxyl groups (DeCanio et al., 1994, Cardona-Martinez and Dumesic, 1992), the temperature of water desorption from Al₂O₃ typically being 600-700 K (Grenoble et al., 1981). Muraki et al. (1991) postulated CO oxidation involves Pt-Al₂O₃ interaction, not specified, with which water might interfere. Analogous to the explanation proposed for the relatively high rates observed at low oxygen partial pressures in the absence of steam, it is more reasonable to assume parallel reaction paths leading to CO₂ in the presence of steam. The fact that the global activation energy estimated is lower than that estimated in the absence of steam can then be explained by a lower activation energy for the second reaction path, resulting in a larger contribution to CO₂ formation of this reaction path at lower temperatures.

The second reaction path most likely includes platinum activating CO while Al₂O₃ sites are the principal sites for water activation. Also, it may be concluded that oxygen and steam interact, since in the absence of oxygen no significant CO₂ production was observed, indicating O₂ chemisorption on Al₂O₃ should be considered. This kind of catalyst bifunctionality, i.e. different sites being responsible for activation of reactants has been reported to be res-

Figure 3.19
Measured and simulated CO₂ production rates vs. P_{CO} in the presence of steam.
Lines: simulation; symbols: experimental.
T = 483 K; P_{O₂} = 2.2 kPa; P_{H₂O} = 10 kPa.
3.7 Conclusions

In this chapter the intrinsic kinetics of the oxidation of CO with oxygen over a Pt/γ-Al₂O₃ catalyst have been addressed over a wide range of experimental conditions using a laboratory fixed bed reactor. It has been established that under these conditions the partial reaction orders in O₂ and CO amount to 1 and -1, respectively. Eight kinetic models have been evaluated; the models best describing the experimental observations were derived assuming a fractional CO coverage close to unity and molecular chemisorption of oxygen being the rate-determining step.

The observed net rates of CO₂ production could be described by

$$\dot{R}_{CO_2} = 2k_{ads}^{O_2} \left( \frac{k_{ads}^{CO}}{A_{des}} \right)^{-1} \exp \left( \frac{-\Delta H_{ads}^{CO}}{RT} \right) \frac{p_{O_2}}{p_{CO}} L_1$$

Mechanistically, this rate expression is based on the following elementary step reaction paths.

Path D

- CO + * → CO*
- O₂ + * → O₂*
- O₂* + * → 2O*
- CO* + O* → CO₂ + 2*
- CO + O* → CO₂ + *

Path C

- 2CO + O₂ → 2CO₂

The values of the kinetic parameter estimated by regression analysis appeared to be physically feasible, the value of the global activation energy amounted to 112 ± 8 kJ mol⁻¹, in agreement with values of ΔH_{des}^{CO} reported in literature for CO covered Pt surfaces. Furthermore, on the basis of the kinetic analysis, it was demonstrated that kinetic models including dissociative adsorption of oxygen in one step are unable to correctly predict the experimental observations.

CO oxidation was found to be enhanced by the presence of steam while the water-gas shift was found to be insignificant under the experimental conditions. The dependence of the CO₂ production rate on the p_{O₂} and p_{CO}, however, was found to be similar to the oxidation in the absence of steam. In addition, the kinetics were found to be virtually independent of the steam partial pressure, except for partial pressures close to zero, hence, the reaction could be described with statistical significance using the aforementioned elementary step reaction.
mechanisms. It was concluded that a reaction path parallel to the aforementioned elementary step model might be responsible for the observed rate enhancement as compared to the reaction in the absence of steam, the importance of both paths in CO$_2$ production being a function of temperature.

References


KINETICS OF CO OXIDATION OVER Pt/γ-Al₂O₃


- Razon L.F., Schmitz R.A., 'Intrinsically unstable behaviour during the oxidation of carbon monoxide on


APPENDIX III

Observed specific CO₂ production rates and corresponding reactant partial pressures and temperatures of experiments used in the regression analysis.

1: Experiments in the absence of steam

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### APPENDIX III

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2: Experiments in the presence of steam, $P_{H_2O} = 10$ kPa

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4

KINETICS OF CO OXIDATION OVER A COMMERCIAL AUTOMOTIVE THREE-WAY CATALYST

4.1 Introduction

Commercial automotive three way catalysts commonly contain considerable amounts of cerium oxide, a base metal oxide added mainly in order to enhance the catalyst's oxidation activity. The role of CeO$_2$ has been described in different terms, depending on the operating environment of the catalyst.

The oxygen storage capacity (Kim, 1982, Lööf et al., 1989, Schlatter and Mitchell, 1980, Su et al., 1985, Kummer, 1986, Herz et al., 1983) of CeO$_2$ can be regarded as a chemical effect: in a flow with oscillating composition oxygen is accumulated during the net oxidising excursions of the oscillation period, while under oxygen deficient conditions this excess oxygen is depleted through reactions with adsorbed CO and hydrocarbons. Hence, under dynamic operating conditions the time-averaged oxidation activity is improved by sustaining the appropriate oxygen stoichiometry in the vicinity of the catalytically active sites. Closely related to this oxygen storage capacity under transient conditions, ceria has been reported to possess oxygen chemisorption sites under steady-state conditions (Jin et al., 1987a, 1987b, Serre et al., 1993b, Nunan et al., 1992a, Oh and Eickel, 1988). In Chapter 3 it has been demonstrated that at temperatures below 500 K the CO oxidation rate on a Pt/Al$_2$O$_3$ catalyst is limited by molecular oxygen chemisorption over a wide range of CO to oxygen ratios in the reactor feed. As a consequence, ceria, providing additional oxygen chemisorption sites, potentially allows the reaction to proceed at a higher rate.

Another chemical effect of CeO$_2$ addition is promoting the water-gas shift reaction at temperatures above light-off (Schlatter, 1978, Schlatter and Mitchell, 1980, Kim, 1982, Herz
and Sell, 1985, Harrison et al., 1988), hence improving the catalyst’s CO conversion activity. This effect was found to occur both under steady state and unsteady state conditions.

Other effects are of a physico-chemical nature: CeO₂ has been claimed to alter the oxidation state of the noble metals in three-way catalysts (Herz and Sell, 1985, Diwell et al., 1991, Nunan et al., 1992a, Tarasov et al., 1988, Lööf et al., 1991b, Zhou et al., 1988) and to stabilise noble metal dispersion at high temperatures (Summers and Ausen 1979, Yao and Yu Yao, 1984, Sanchez and Gazquez, 1987, Murrell et al., 1991, Chojnacki et al., 1991). In addition, ceria addition was found to improve the thermal stability of the catalyst (Harrison et al., 1988). These physico-chemical aspects of the interaction between ceria and noble metals are sometimes referred to as strong metal-support interactions (SMSI) (Yao et al., 1980, Munuera et al., 1991).

The role of ceria remains a widely studied subject, but no unambiguous explanation of the role of ceria in CO oxidation has been provided, in particular due to the sensitivity of the experimental results towards catalyst pretreatment, experimental procedures and operating conditions (Engler et al., 1989). Moreover, many explanations for the effects of ceria on CO oxidation activity pertain to the non-steady state, e.g., the noble metal catalyzed reduction of ceria (Yao and Yu Yao, 1984, Jin et al., 1987a, Serre et al., 1993a) has been reported to account for increased CO oxidation activity (Serre et al., 1993a, 1993b, Nunan et al., 1992a). These effects are of a transient nature, and do not reflect the intrinsic role of ceria under steady state conditions.

One of the most interesting features of ceria addition to automotive three-way catalysts is its influence on the CO oxidation activity in the presence of steam since steam is abundant under all conditions encountered in practical use. Beneficial effects are generally assigned to the water gas shift reaction even at low temperatures, while it was found that temperatures over 670 K were required for this reaction to occur at a substantial rate (Schlatter, 1978, Kim, 1982).

Because of the lack of unambiguous explanations for the effect of CeO₂ on the CO oxidation rate, the influence of ceria on the oxidation of CO in the absence and in the presence of steam is examined in this Chapter at temperatures between 400 and 500 K. This study was carried out using both ceria promoted and unpromoted γ-Al₂O₃ supported Pt, Rh and Pt/Rh catalysts. Given the importance of automotive emissions at temperatures below light-off, the influence of the process conditions on the oxidation of CO over the commercial Pt/Rh/CeO₂/Al₂O₃ catalyst was studied in more detail.

From a mechanistic point of view it is important to determine the role of steam as a potential source of oxygen in the oxidation of CO in the presence of dioxygen, a matter that has drawn little attention so far, see Barbier and Duprez (1994) for a recent review on steam effects in automotive exhaust catalysis. From steady-state experiments it is not possible to distinguish between the contribution of O₂ and H₂O in the oxidation process. Hence, steady-state isotopic transient kinetic experiments were performed to supplement steady state experiments (Happel, 1986).
4.2 Experimental

Catalyst

All catalyst samples were provided by Degussa AG, and contained 0.398 w% Pt and/or 0.0798 w% Rh and/or 28 w% CeO₂, corresponding to 2.04 \times 10^{-2} \text{ mol kg}_{c}^{-1} \text{ Pt}, 7.83 \times 10^{-3} \text{ mol kg}_{c}^{-1} \text{ Rh} and 1.65 \text{ mol kg}_{c}^{-1} \text{ CeO₂}. The specific surface areas of Al₂O₃ and CeO₂ amounted to 190 m² g⁻¹ and 20 m² g⁻¹, respectively. Prior to experiments the catalysts, diluted with inert nonporous \alpha-\text{Al}_2\text{O}_3, were pretreated as described in section 2.5.

Chemisorption

The Pt, and Rh catalysts have been characterised by means of standard static CO chemisorption measurements at a temperature of 308 K, as described in section 2.5. Both CeO₂ promoted and unpromoted catalysts were used. The CO chemisorption characteristics of the commercial Pt/Rh/CeO₂/Al₂O₃ catalyst were studied as follows, using a single catalyst sample. After a standard measurement, see section 2.5, CO chemisorption was measured at 308, 348, 398 and 473 K. Each experiment following the standard measurement was preceded by the in situ pretreatment procedure listed in Table 4.1. The series of chemisorption experiments was completed by a standard chemisorption experiment. CO chemisorption on the CeO₂/Al₂O₃ support was studied at 308 and 473 K. Each chemisorption experiment, including the in situ pretreatment, took 6 to 12 hours, the latter being typical for the standard experiment.

Due to the uncertainty of the CO chemisorption stoichiometry on Al₂O₃ and CeO₂/Al₂O₃ supported noble metal catalysts, calculation of the fraction exposed noble metal from chemisorption data may be questionable. Nevertheless, in order to allow comparison of measured rate data the fraction exposed noble metal has been calculated from CO chemisorption at 308 K, assuming chemisorption stoichiometries of 1 CO per Pt atom and 2 CO per Rh atom. It was verified that at this temperature no significant CO chemisorption on the support occurred.
Prior to the kinetic measurements the catalyst was lined out according to the procedure described in the line-out section in Chapter 3. Steady-state kinetic measurements were performed as described in section 3.2.

The effect of CeO$_2$ on the oxidation of CO both in the absence and in the presence of steam was examined by means of a comparative study using model catalysts and the commercial Pt/Rh/CeO$_2$/Al$_2$O$_3$ catalyst at a 463 K and a CO inlet partial pressure of 2.2 Kpa. With each catalyst batch the CO$_2$ production rate was measured at a steam inlet partial pressure of 10 kPa using a reducing, a stoichiometric and an oxidising mixture, based on the CO to oxygen ratio in the feed. Subsequently, the same sequence of experiments was carried out in the absence of steam. Catalysts used and the process conditions applied are listed in Table 4.2. Note that, in order to account for the different activities of the catalysts, the amount of catalyst in the reactor was varied, the amount of relatively low loaded Rh/Al$_2$O$_3$ being 12.5 times larger than the amount of the commercial catalyst. Since it was confirmed that experiments were performed under differential conditions on the commercial catalyst, see Figure 4.4, it was assumed that the resulting difference in space-time did not affect the measured CO$_2$ production rates.

**Table 4.2**

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The effects of the process conditions on CO oxidation over the commercial Pt/Rh-/CeO$_2$/γ-Al$_2$O$_3$ catalyst were studied under the conditions listed in Table 4.3.

Steady state isotopic transient experiments were performed using the commercial Pt/Rh/CeO$_2$/γ-Al$_2$O$_3$ catalyst, the experimental conditions are shown in Table 4.4, and were carried out as follows. After catalyst line-out the desired process conditions were set and the steady state CO$_2$ production rate was measured by GC analysis of the reactor effluent. After this measurement an isotopic transient was introduced by an abrupt switch between feed-streams containing either $^{16}$O$_2$ and $^{18}$O$_2$ or $H_2^{16}$O and $H_2^{16}$O/$H_2^{18}$O while the rest of the feed...
stream remained unchanged. In this way, the evolution of isotopically labelled reactant and products could be measured using the quadrupole mass spectrometer, see section 2.4, without perturbing the steady state. Argon was used as an inert tracer. The gases used in steady state experiments are CO (99.997%), O₂ (99.999%) and H₂O (deionised) as reactants. In addition, in steady state isotopic transient experiments, ¹⁸O₂ (96%), and H₂¹⁸O (10 mol% in H₂¹⁶O) were used. He (99.9990%) was used as balance in all experiments.

### Effects potentially interfering with intrinsic kinetic measurements

After the in situ line-out procedure described in section 3.2, the ceria containing catalyst samples could be used for kinetic measurements for at least two days. On a longer timescale the CO oxidation activity of these catalysts decreased, in contrast with the Pt/γ-Al₂O₃ catalyst described in Chapter 3.

Reproducibility of the experiments was confirmed by duplicating an experiment using different catalyst batches: the measured CO₂ production rates varied within the experimental error.

The axial temperature increase measured over the catalyst bed was typically smaller than 2 K. Therefore, the influence of axial temperature gradients on the net CO₂ production rate was considered negligible.

The influence of the other potential heat and mass transport limitations has been evaluated for each CO₂ production rate measured, as illustrated in Chapter 2, Appendix II. Only intrinsic kinetic data acquired after at least 10 ks on stream were selected for the kinetic analysis.
4.3 Results

4.3.1 Chemisorption

The results of the standard chemisorption experiments are listed in Table 4.5. \( n_{ads} \) denotes the amount of CO adsorbed after the first isotherm was taken, \( n_{chem} \) denotes the amount of CO chemisorbed, calculated as the difference between the amounts adsorbed during the first analysis and the repeat analysis, and \( n_{NM} \) denotes the amount of noble metal in units of mol kg\(^{-1}\). The amount of CO chemisorbed per mole of noble metal on the ceria containing catalysts was larger than that on the ceria-free samples by a factor of 2.2 for the Pt and Rh samples, and by a factor of 1.4 for the Pt/Rh samples. Since the CeO\(_2\)/Al\(_2\)O\(_3\) support did not show significant CO chemisorption at 308 K, this may be explained by an increased fraction exposed noble metal on ceria containing catalysts. The corresponding fractions of exposed metal atoms for the monometallic catalysts were calculated using the chemisorption stoichiometries described in the previous section. Calculation of \( FE \) in the bimetallic catalysts is not straightforward, because the CO adsorption stoichiometries of Pt and Rh differ. Since the amount of CO chemisorbed on the Pt/Rh/Al\(_2\)O\(_3\) catalyst, \( n_{chem} \) in Table 4.5, was equal to the sum of the amounts chemisorbed on the Pt/Al\(_2\)O\(_3\) and Rh/Al\(_2\)O\(_3\) catalysts it was assumed that the fractions of exposed Pt and Rh atoms in Pt/Rh/Al\(_2\)O\(_3\) were equal to those in the corresponding monometallic catalysts. The fraction of exposed noble metal atoms is then calculated as the weighted average of the fractions of exposed noble metals of the monometallic catalysts. This indicates that Pt and Rh in the Pt/Rh/Al\(_2\)O\(_3\) catalyst do not mutually influence CO chemisorption. For the Pt/Rh/\( \text{CeO}_2\)/Al\(_2\)O\(_3\) catalyst this does not hold, the amount of CO chemisorbed being smaller than the sum of the amounts chemisorbed on

\begin{table}[h]
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\begin{tabular}{|c|c|c|c|c|c|}
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Catalyst & \( n_{ads} \) & \( n_{chem} \) & \( n_{chem}/n_{NM} \) & \( FE \) & \( L_{NM} \) \\
 & \( /10^3 \text{ mol kg}^{-1} \) & \( /10^3 \text{ mol kg}^{-1} \) & \( /\text{mol mol}_{NM}^{-1} \) & & \( /10^3 \text{ mol kg}^{-1} \) \\
\hline
Pt/Al\(_2\)O\(_3\) & 26 & 7.9 & 0.39 & 0.39 & 8.0 \\
Rh/Al\(_2\)O\(_3\) & 25 & 8.1 & 1.04 & 0.52 & 4.1 \\
Pt/Rh/Al\(_2\)O\(_3\) & 32 & 16 & 0.58 & 0.42 & 12.1 \\
Pt/\( \text{CeO}_2\)/Al\(_2\)O\(_3\) & 38 & 17 & 0.83 & 0.83 & 17.0 \\
Rh/\( \text{CeO}_2\)/Al\(_2\)O\(_3\) & 41 & 18 & 2.3 & 1.0 & 7.8 \\
Pt/Rh/\( \text{CeO}_2\)/Al\(_2\)O\(_3\) & 42 & 23 & 0.81 & 0.64 & 18.0 \\
\( \text{CeO}_2\)/Al\(_2\)O\(_3\) & 0.0 & 0.0 & - & - & - \\
\hline
\end{tabular}
\caption{CO chemisorption capacities and corresponding fractions and concentrations of exposed metal atoms after the in situ pretreatment according to Table 2.5.}
\end{table}

the Pt/\( \text{CeO}_2\)/Al\(_2\)O\(_3\) and Rh/\( \text{CeO}_2\)/Al\(_2\)O\(_3\) catalysts. From the amount of chemisorbed CO on the bimetallic catalyst it is not possible to distinguish between CO chemisorbed on Pt and on
Rh without additional information, therefore it was assumed that the fractions of exposed Pt and Rh were equal.

From the fractions of exposed metal atoms and the noble metal loadings the specific concentration of exposed noble metal atoms, \( L_{NM} \), was calculated in order to allow comparison of the observed turnover frequencies.

Although the specific surface area of CeO\(_2\) is smaller than that of Al\(_2\)O\(_3\) by an order of magnitude, the large amounts of CO chemisorbed on the CeO\(_2\) containing samples in comparison with the ceria-free catalysts indicate that most of the noble metal is located on the ceria surface. The observed CO/Rh ratio of 2.3 for the ceria containing Rh catalyst indicates that on Rh CO is primarily chemisorbed as Rh gem-dicarbonyl (Keiski et al., 1994).

The CO chemisorption capacities of the Pt/Rh/CeO\(_2\)/Al\(_2\)O\(_3\) catalyst and the CeO\(_2\)/Al\(_2\)O\(_3\) support, measured as a function of the sorption temperature and after pretreatment at two different temperatures, are listed in Table 4.6. The main difference between a pre-treatment temperature of 773 K and 473 K is that the amount of weakly held CO, \( n_{ads} - n_{chem} \), is negligible after the low temperature pretreatment. The amount of CO chemisorbed does not vary appreciably as a function of temperature at temperatures below 400 K, also indicating that the pretreatment at 473 K is sufficient to remove irreversibly chemisorbed CO from a previous measurement.

CO chemisorption at 473 K led to a drastic increase of both the amount of CO chemisorbed and the amount of CO weakly bonded, the amount of CO chemisorbed clearly exceeding the amount of noble metals present in the sample. Since the catalyst had been reduced in hydrogen at 473 K, not higher, it is reasonable to assume that exposure to CO during 10 ks at this temperature led to additional reduction of ceria by formation of formate and carbonate species. This is substantiated by the uptake of CO by the CeO\(_2\)/Al\(_2\)O\(_3\) support under the same conditions. The fact that the amount chemisorbed on the support is smaller than the extra CO uptake by the Pt/Rh/CeO\(_2\) catalyst compared to the Pt/Rh/Al\(_2\)O\(_3\) catalyst is explained by the enhanced reducibility of ceria in the presence of noble metals (Yao and Yu-Yao, 1984, Serre et al., 1993b).

| Table 4.6 |
| CO chemisorption capacities of Pt/Rh/CeO\(_2\)/Al\(_2\)O\(_3\) and CeO\(_2\)/Al\(_2\)O\(_3\) at different temperatures. Pretreatment I: chemisorption after in situ pretreatment at 773 K, according to Table 2.5; pretreatment II: chemisorption after in situ pretreatment at 473 K, according to Table 4.1. |

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<th>( n_{chem} ) /10(^2) mol kg(_c)(^{-1})</th>
<th>( n_{chem}/n_{NM} ) mol mol(_{NM}^{-1})</th>
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<tr>
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<td>II</td>
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<td>15</td>
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<tr>
<td>348</td>
<td>II</td>
<td>20</td>
<td>20</td>
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<tr>
<td>398</td>
<td>II</td>
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<td>19</td>
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</tr>
<tr>
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<td>II</td>
<td>70</td>
<td>62</td>
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<tr>
<td>473</td>
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<td>473</td>
<td>I</td>
<td>40</td>
<td>20</td>
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</table>
4.3.2 Effect of ceria on the oxidation of CO over γ-alumina supported Pt, Rh and Pt/Rh catalysts

Figure 4.1 shows the specific CO₂ production rate, *i.e.* in units of mol kg⁻¹ s⁻¹, as a function of the oxygen partial pressure using a CeO₂ promoted and an unpromoted Pt/Rh/Al₂O₃ catalyst, both in the presence and in the absence of steam. The experimental conditions are listed in Table 4.2. The presence of ceria greatly enhances the CO₂ production rate under the conditions applied, the effect being more pronounced in the presence of steam. It was verified that the CeO₂/Al₂O₃ support did not show significant CO oxidation activity under the experimental conditions. Moreover, since no hydrogen production was observed in the presence of steam, the contribution of the water-gas shift reaction to the enhanced CO₂ production rates in the presence of steam was considered negligible.

Figure 4.2 shows the CO₂ production rate using a ceria promoted and unpromoted Pt/Al₂O₃ catalyst under the same experimental conditions. The results for the ceria promoted and unpromoted Rh/Al₂O₃ catalysts are shown in Figure 4.3.

Comparison of Figures 4.1 and 4.2 indicates that the rate enhancements in the presence of ceria for the Pt/Al₂O₃ catalyst are comparable to those observed for the Pt/Rh/Al₂O₃ catalyst. With the Rh/Al₂O₃ catalyst, Figure 4.3, the rate enhancement by ceria is significantly higher than for the Pt containing catalyst, but the specific rates are smaller compared to the platinum containing catalysts. Steam does not affect the oxidation rate over the Rh/Al₂O₃ nor over the Rh/CeO₂ catalysts. Hence, it is inferred that, under the experimental conditions,
the CO oxidation activity of the commercial Pt/Rh/CeO₂/Al₂O₃ catalyst is dominated by platinum.

Figures 4.1 to 4.3 clearly show that the partial reaction orders in O₂ for all ceria containing catalysts are smaller than unity, i.e. the partial reaction order for the ceria-free catalysts, see Chapter 3. As a result, the rate enhancements observed for the ceria containing catalysts decrease when going from net reducing to oxidising conditions.

In Table 4.7 the rate enhancements by ceria are listed, expressed as the ratio of the specific CO₂ production rates for the ceria promoted and unpromoted catalysts and calculated from Figures 4.1 to 4.3. Comparing the rate enhancements from Table 4.7 to the concentrations of exposed metal for the ceria promoted and unpromoted catalysts, see Table 4.5, shows that the rate enhancements cannot be solely attributed to the increased concentration of exposed noble metal atoms in the ceria promoted catalysts.

A comparison of the specific CO₂ production rates observed for the Pt/Al₂O₃ and Rh/Al₂O₃ catalysts shows that the latter are typically smaller by a factor of 7, see Figures 4.2 and 4.3, while Table 4.5 shows the concentration of exposed Pt is approximately only twice as large as that of Rh. Hence, the turn-over frequencies between both catalysts typically differ by a factor of 3.5. In the presence of ceria, however, the difference in CO₂ production rates obtained for both catalysts is markedly smaller: the observed turnover frequencies for the Pt/CeO₂/Al₂O₃ catalyst are less than 50% larger than for the Rh/CeO₂/Al₂O₃ catalyst.

Table 4.7
Rate enhancement by ceria as observed for Al₂O₃ supported Pt, Rh and Pt/Rh catalysts in the absence and in the presence of steam. The rate enhancement is expressed as the ratio of Rₓ,CO₂ measured over the ceria promoted and unpromoted catalyst. Conditions: T = 463 K; P₇₀ = 2.2 kPa.

<table>
<thead>
<tr>
<th>P_/P₂</th>
<th>P/H₂O = 0</th>
<th>P/H₂O = 10 kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt</td>
<td>Rh</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>26</td>
</tr>
<tr>
<td>2</td>
<td>9</td>
<td>19</td>
</tr>
<tr>
<td>0.5</td>
<td>5</td>
<td>9</td>
</tr>
</tbody>
</table>
4.3.3 Influence of process variables on CO₂ production rate using a commercial Pt/Rh/CeO₂/Al₂O₃ catalyst

**Space time**

The experiments using the Pt/Rh/CeO₂/γ-Al₂O₃ catalyst have been carried out under differential operating conditions. The influence of space time on the CO₂ production rate is then negligible, as has been shown in section 2.2. Figure 4.4 shows the conversion of CO versus the space time of CO, $W/F_{CO,0}$, validating the assumption of differential reactor operation. $X_{CO}$ is directly proportional to $W/F_{CO,0}$ at least until $X_{CO}$ equals 15%. In all experiments the space time has been manipulated as to obtain CO conversions between 1% and 15%.

**Assessment of the importance of the water-gas shift reaction**

Experiments were carried out using the commercial Pt/Rh/CeO₂/Al₂O₃ catalyst at different temperatures using feed mixtures containing varying amounts of CO and steam. In order to estimate the importance of the water-gas shift reaction, the CO oxidation rate due to water-gas shift was compared to typical oxidation rates measured in the presence of oxygen and steam. A mixture containing 5 kPa CO and 10 kPa steam was fed to the reactor in the absence of oxygen. At 600 K significant amounts of hydrogen were produced. Corresponding CO₂ production rates of typically $10^{-3}$ mol kg⁻¹ s⁻¹ were observed, whereas typical CO₂ production rates measured in the presence of both steam and oxygen were in the order of $10^{-2}$ mol kg⁻¹ s⁻¹ at a temperature as low as 413 K. Since the apparent activation energy for the water-gas shift reaction obtained from an Arrhenius plot amounted to 60 kJ mol⁻¹ between 500 and 600 K, the water-gas shift reaction can be considered insignificant at temperatures between 400 and 500 K.

**Influence of oxygen partial pressure**

In addition to Figure 4.1, Figure 4.5 shows in more detail the influence of the oxygen partial pressure on the oxidation of CO over a Pt/Rh/CeO₂/Al₂O₃ catalyst. The experiment was performed in the presence of steam at 413 K. In the absence of steam, the dependence of $R_w$ on the oxygen partial pressure is qualitatively similar, see Figure 4.1. Only CO₂ was found as a reaction product, i.e. no H₂ was detected, indicating the reaction of CO and O₂ in
the presence of steam can be regarded as
stoichiometrically single.

In the absence of oxygen, no CO$_2$ was formed
under steady state conditions, confirming the insignifi-
cance of the water-gas shift reaction. Apparently, a
relatively small amount of oxygen in the feed gas is
sufficient to establish a substantial CO oxidation rate.
Note that the rates measured in the presence of steam at
a temperature of 413 K are comparable to those
measured in the absence of steam at 463 K, see Figure
4.1. These results indicate that, even though no net
consumption of steam occurs, steam plays an important
role in the oxidation of CO, but only if oxygen is present
in the reactor feed.

Influence of CO partial pressure

Figure 4.6 shows the CO$_2$ production rate as a
function of the CO partial pressure in the absence of steam. At a temperature of 463 K the rate initially decreases on increasing the CO partial pressure, until the CO to oxygen ratio in the feed gas approaches unity. This behaviour resembles the negative partial reaction order in CO of the Pt/Al$_2$O$_3$ catalyst at the same temperature, see Figure 3.3. At increasing $p_{CO}$ or decreasing temperature, however, the partial reaction order in CO approaches zero.

Figure 4.7 shows the CO$_2$ production rate versus the oxygen partial pressure at three
different CO partial pressures. The CO$_2$ production rate is not sensitive to the CO partial
pressure, which is in agreement with Figure 4.6. Figure 4.8 shows the CO$_2$ production rate as a
function of the CO partial pressure
in a mixture containing steam. As opposed to experiments carried out
in the absence of steam, no signifi-
cant negative partial reaction order in CO is observed. In Chapter 3 it
was demonstrated that the negative
partial reaction order in CO could be attributed to rate inhibition by
CO adsorbed on platinum. Hence,
from Figure 4.8 it follows that
under the experimental conditions
no significant CO inhibition occurs.
Influence of steam partial pressure

In the preceding section it was shown that both steam and oxygen are essential for CO oxidation to occur at a substantial rate. In Figure 4.9 the CO₂ production rate is shown as a function of the H₂O partial pressure at a temperature of 413 K. Increasing the H₂O partial pressure increases the CO₂ production rate, the effect being largest at low H₂O partial pressures. No rate inhibition by steam occurs, even if relatively large amounts of steam, up to 12 vol%, are present in the feed gas.

Influence of CO₂ partial pressure

Figure 4.10 shows the influence of adding CO₂ to reactant mixture in the absence and in the presence of steam. Note that the curves were obtained from experiments performed at different temperatures of 443 K and 413 K, respectively. The presence of small amounts of CO₂ in the feed gas lowers the CO₂ production rate. The absolute
decrease in net CO₂ production rates are similar in the presence and in the absence of steam in the feed gas; the relative decrease of \( R_w \) is larger in the absence of steam.

This decrease in net CO₂ production rate has not been observed for the Pt/Al₂O₃ catalyst, as described in Chapter 3, where it was concluded from kinetic modeling that CO₂ desorption from Pt/Al₂O₃ is irreversible. From Figure 4.10 it follows that CO₂ desorption can not be considered irreversible on ceria containing catalysts.

**Effect of temperature**

Figure 4.11 shows the effect of temperature on the CO oxidation rate, for a feed corresponding to 2.2 kPa CO and 1.1 kPa O₂. Two temperature ranges can be discerned with two corresponding distinct apparent activation energies. At temperatures between 393 and 433 K the apparent activation energy amounts to 26 kJ mol⁻¹, at higher temperatures to 56 kJ mol⁻¹. This indicates that parallel reaction paths towards CO₂ exists. In the presence of steam a constant apparent activation energy amounting to 48 kJ mol⁻¹ was found over the entire temperature range.
4.3.4 Step changes in isotopic compositions using a $\text{Pt/Rh/Ce}_0\text{O}_2/\gamma-\text{Al}_2\text{O}_3$ catalyst

Step change $^{16}\text{O}_2/^{18}\text{O}_2$ in the absence of steam

In order to allow a comparison between CO oxidation in the absence and in the presence of steam, a steady state isotopic transient experiment was carried out in the absence of steam at a temperature of 413 K using a reactant mixture containing 0.9 kPa of dioxygen and 2.9 kPa of CO. Prior to the experiment the catalyst had been exposed to the reaction mixture for 60 ks and the steady state CO$_2$ production rate amounted to $9.3 \times 10^{-4}$ mol kg$_\text{c}$s$^{-1}$.

After switching from $^{16}\text{O}_2$ to $^{18}\text{O}_2$, the product gas contained $^{16}\text{C}_2\text{O}_2$, $^{16}\text{C}_2\text{O}^{18}\text{O}$ and $^{18}\text{C}_2\text{O}_2$ but no significant amount of $^{18}\text{O}^{18}\text{O}$. The fraction $^{16}\text{C}_2\text{O}^{18}\text{O}$ increased very slowly after switching, while $^{18}\text{C}_2\text{O}_2$ was produced at a rate smaller than that of $^{16}\text{C}_2\text{O}^{18}\text{O}$ by an order of magnitude. When the fraction of $^{16}\text{C}_2\text{O}^{18}\text{O}$ in CO$_2$ amounted to 0.4, a switch back was made to $^{16}\text{O}_2$. The resulting responses of $^{18}\text{O}_2$ and $^{16}\text{C}_2\text{O}^{18}\text{O}$ are shown in Figure 4.12.

The responses of $^{18}\text{O}_2$ and argon virtually coincide, indicating oxygen chemisorption is irreversible. The $^{16}\text{C}_2\text{O}^{18}\text{O}$ response significantly lags that of argon, demonstrating that CO$_2$ is formed via oxygen containing surface species, the shape of the $^{16}\text{C}_2\text{O}^{18}\text{O}$ transient indicates the formation proceeds $via$ only one significant kind of surface species (Happel, 1986). The average surface lifetime $\tau$ of the $^{18}\text{O}$ intermediate leading to CO$_2$ is determined from the area between the $^{16}\text{C}_2\text{O}^{18}\text{O}$ and Ar transients, the latter being a measure of the gas phase hold-up, and amounts to 300 s. The maximum surface concentration $L^{\text{max}}$ of the $^{18}\text{O}$ intermediate leading to CO$_2$, in units of mol kg$_\text{c}$s$^{-1}$, is calculated by dividing $\tau$ by the space time of $^{16}\text{C}_2\text{O}^{18}\text{O}$ and amounts to 0.3 mol kg$_\text{c}$s$^{-1}$. $L^{\text{max}}$ is not significantly biased by CO$_2$ readsoption since the average surface lifetime is orders of magnitude larger than the residence time in the reactor, approximately $10^2$ s. In addition, the CO$_2$ partial pressure due to reaction is small, typically $10^{-2}$ kPa; from Figure 4.10 it follows that this partial pressure of CO$_2$ does not significantly affect the CO$_2$ production rate.

Isotopic exchange between oxygen and steam

Assessment of the role of the potential oxygen sources for CO$_2$ production, i.e. dioxygen and steam, through isotopically labelled oxygen is only feasible if no significant
exchange of oxygen atoms between dioxygen and steam occurs in the absence of CO. This was verified experimentally by means of an oxygen exchange experiment: negligibly small amounts of $^{16}\text{O}^{18}\text{O}$ and $\text{H}_2^{18}\text{O}$ were found in the absence of CO after a step change from $^{16}\text{O}_2/\text{H}_2^{16}\text{O}$ to $^{18}\text{O}_2/\text{H}_2^{16}\text{O}$.

Step change $^{16}\text{O}_2/^{18}\text{O}_2$ in the presence of steam

After a step change from $^{16}\text{O}_2$ to $^{18}\text{O}_2$ the steady state production rates of the isotopes of CO$_2$ were measured after the isotopic transients had relaxed. Figure 4.13 shows the steady-state production rates of C$^{16}$O$_2$, C$^{16}$O$^{18}$O and H$^{18}$O at two dioxygen partial pressures. Note that, except for the fact that steam is present, the conditions include those of the experiment shown in Figure 4.12. The conditions were such that the amounts of labelled and unlabelled oxygen entering the reactor via dioxygen and steam were of comparable magnitude.

The amount of oxygen atoms in ceria amounts to approximately 3 mol kg$^{-1}$Ce, from which it can be calculated that, at a C$^{16}$O$_2$ production rate of 9 $10^{-3}$ mol kg$^{-1}$Ce s$^{-1}$, it would take 333 s to deplete all $^{16}$O from CeO$_2$. The fact that a steady-state production rate of C$^{16}$O$_2$ of 9 $10^{-3}$ mol kg$^{-1}$Ce s$^{-1}$ was measured for over 400 s indicates that $^{16}$O originating from $\text{H}_2^{16}\text{O}$, rather than lattice oxygen from CeO$_2$, plays an important role in the reaction. If this were not the case, the formation of C$^{16}$O$_2$ would cease after the $^{16}$O atoms of CeO$_2$ had been fully consumed by CO.

Approximately 85% of CO$_2$ is produced as C$^{16}$O$_2$, 15% as C$^{16}$O$^{18}$O, while less than 0.1 % C$^{18}$O$_2$ was formed. Since no $^{16}$O$_2$ was fed to the reactor and the lattice oxygen of CeO$_2$ does not contribute significantly to the production of CO$_2$, these numbers indicate that the majority of CO$_2$ produced contains oxygen atoms originating from steam rather than from O$_2$. Note that the production rate of C$^{16}$O$^{18}$O in the presence of steam is similar to that in the absence of steam, while H$^{18}$O is produced at a rate equal to that of C$^{16}$O$_2$.

From the fact that no H$_2$ or any other hydrogen containing products were observed it can be concluded that no
net consumption of H₂O occurs. These results show that, although no net disappearance of H₂O occurs, steam is involved in the oxidation of CO: for each mole of CO₂ containing oxygen atoms from H₂O a mole of H₂O containing oxygen atoms from O₂ is formed.

Increasing the dioxygen partial pressure results in an increased CO₂ production rate, as was shown in Figure 4.5. Figure 4.13 shows that this increase is primarily due to an increase in the production rates of C¹⁶O₂ and H₂¹⁸O. Upon switching off the steam supply, the production rates of C¹⁶O₂ and H₂¹⁸O decayed analogously to the steam flow rate, whereas the C¹⁶O¹⁸O production rate was hardly affected.

Figure 4.14 shows the steady-state production rates of C¹⁶O₂, C¹⁶O¹⁸O and H₂¹⁸O at two steam partial pressures, analogous to Figure 4.9. The increasing rate at increasing pH₂O is, again, dominated by an increasing C¹⁶O₂ production rate. Comparing the production rates of C¹⁶O¹⁸O from Figures 4.13 and 4.14 shows that this rate is more sensitive to changes in the partial pressure of O₂ than to that of steam.

Figure 4.15 shows the transient response of O₂, H₂O, C¹⁶O¹⁸O and argon after a step change from O₂ to O₂. The responses of Ar and O₂ are similar while the response of C¹⁶O¹⁸O significantly lags the argon response. The initial slope of the response curve of H₂¹⁸O is zero indicating this species is formed via more than one significant oxygen containing surface species. The average surface residence times of the O₂ intermediates in the presence of steam are an order of magnitude smaller than those in the absence of steam, compare Figures 4.12 and 4.15.

After a step change from H₂¹⁶O to H₂¹⁶O containing 10 mol% of H₂¹⁸O the steady state production rates of the isotopes of CO₂ were measured after the isotopic transients had relaxed. Figure 4.16 shows the steady-state production rates of C¹⁶O₂, C¹⁶O¹⁸O and their sum as a function of the steam partial pressure. The fraction C¹⁶O¹⁸O decreases slightly, from
15.3% for the lowest to 13.9% for the highest steam partial pressure considered. Less than 1% of CO$_2$ was produced as C$^{18}$O$_2$.

Figure 4.17 shows the responses of C$^{16}$O$^{18}$O and H$_2^{18}$O after a step change from the mixture containing unlabelled to a mixture containing labelled steam. The response of C$^{16}$O$^{18}$O follows the argon response until its flow rate amounts to approximately 55% of its maximum value, while the response of H$_2^{18}$O lags the argon signal. The observation that H$_2^{18}$O formed by reaction, see Figure 4.15, relaxes more slowly than H$_2^{18}$O which is fed to the reactor indicates that the relaxation of the former is due to reaction rather than to readsoption. H$_2^{18}$O formed by reaction also relaxes more slowly than C$^{16}$O$^{18}$O in Figure 4.17, which is CO$_2$ formed through reaction of CO with H$_2^{18}$O. This indicates that formation of H$_2$O proceeds via stronger interaction with the surface than formation of CO$_2$.

![Figure 4.16](image)

**Figure 4.16**
Steady state production rates of (+) total CO$_2$; (a) C$^{16}$O$_2$ and (b) C$^{16}$O$^{18}$O versus p$_{H_2O}$ using the Pt/Rh/CeO$_2$/$\gamma$-Al$_2$O$_3$ catalyst. Conditions: p$_{CO}$ = 2.2 kPa; p$_{O_2}$ = 1.7 kPa; T = 413 K.

![Figure 4.17](image)

**Figure 4.17**
Responses of Ar, C$^{16}$O$^{18}$O and H$_2^{18}$O versus time after a step from H$_2^{16}$O to 90% H$_2^{16}$O/10% H$_2^{18}$O using the Pt/Rh /CeO$_2$/$\gamma$-Al$_2$O$_3$ catalyst. Conditions: p$_{CO}$ = 2.2 kPa; p$_{H_2O}$ = 2.9 kPa; T = 413 K.

### 4.4 Discussion

**Fraction of exposed metal atoms**

The higher fraction of exposed metal of the CeO$_2$ promoted catalysts in comparison with the unpromoted catalysts, see Table 4.5, is in agreement with the observation of Diwell et al. (1991) and Yao and Yu-Yao (1984). This phenomenon has been attributed to the formation of isolated noble metal atoms or small clusters that occupy oxygen vacancies on the ceria surface (Sanchez and Gazquez, 1987). The assumption that most of the noble metal...
is located on the ceria surface is in agreement with the observation of Yao and Kummer (1987), Lööf et al. (1991a), Shyu and Otto (1989), and Nunan et al. (1992a). Hence, the observation that the fraction of exposed noble metal atoms for the CeO₂ promoted Pt/Rh catalyst is smaller than those of the monometallic catalysts may be due to the small surface area of ceria (Murrell et al., 1991).

It follows from Table 4.6 that the major difference in CO adsorption on catalysts reduced at 773 K and 473 K was that the amount of weakly held CO on the latter was negligible. Since reduction at 773 K is likely to have produced more oxygen vacancies (Herrmann et al., 1989), this effect may be attributed to the absence of CO adsorbed linearly on surface oxygen vacancies in ceria, because these vacancies are suitable sites for such species (Li et al., 1989a, 1989b). Additionally, according to the same authors, all other chemisorbed species identified on ceria are stable at room temperature in vacuo.

Effect of ceria on the oxidation of CO in the absence of steam

The CO₂ production rates for the ceria supported catalysts were found to be larger than those for the unpromoted catalysts by a factor of 5 to 26, see Table 4.7, while the CeO₂/Al₂O₃ support did not show significant catalytic activity. It was demonstrated that the larger fraction of exposed noble metal sites on ceria containing catalyst compared to ceria-free catalysts could not account for the observed rate enhancement by ceria. Table 4.8 shows a reaction mechanism, containing two parallel reaction paths, that is qualitatively consistent with the experimental results.

The observed CO inhibition at a temperature of 463 K, see Figure 4.6, indicates that the monofunctional reaction path consisting of reactions 1 to 4 in Table 4.8, plays a role in the oxidation of CO over ceria promoted catalysts. There exists sufficient evidence that the chemisorption characteristics of CO and oxygen on alumina supported noble metal catalysts are not significantly modified by ceria (Zafiris and Gorte, 1992, 1993b, Oh and Eickel, 1988). Therefore, it can be reasonably assumed that this monofunctional reaction path is similar to the mechanism for CO oxidation over a Pt/Al₂O₃ catalyst discussed in Chapter 3, showing that under the experimental conditions the noble metal particles in CeO₂ promoted catalysts are primarily covered by CO, similar to unpromoted catalysts. Clearly, reactions 1 to 4 in Table 4.8 cannot account for the observed rate enhancement by ceria, and neither does this reaction path predict a temperature dependence as shown in Figure 4.11.

Reaction path II Table 4.8 represents a bifunctional reaction path parallel to the monofunctional reaction path, which shows the effect of ceria on the oxidation of CO in a straightforward way. The reaction path is considered bifunctional because ceria provides oxygen chemisorption sites, while CO only chemisorbs significantly on noble metal particles. As a result, oxygen chemisorption is no longer inhibited by CO chemisorbed on noble metal sites, so the latter does no longer affect the CO₂ production rate. The importance of this mechanism is substantiated experimentally by the observed reaction order of zero in CO at temperatures up to 443 K, see Figure 4.6, while the reaction still proceeds at a substantial rate.
Table 4.8
Reaction mechanism for CO oxidation in the absence of steam on ceria promoted noble metal catalysts. Reaction path I describes the monofunctional reaction path, see Chapter 3; path II includes oxygen chemisorption on ceria followed by two successive reactions of oxygen with CO. ‘*’ denotes a vacant site on the exposed noble metal surface; ‘s’ denotes a vacant site on the ceria surface.

<table>
<thead>
<tr>
<th>Reaction Step</th>
<th>Mechanism</th>
<th>Path I</th>
<th>Path II</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CO + * ⇄ CO*</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>O₂ + * → O₂*</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>O₂* + * → 2O*</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>CO* + O* → CO₂</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>O₂ + s → O₂s</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>6</td>
<td>CO* + O₂s → CO₂ + Os + *</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>7</td>
<td>CO* + Os → CO₂ + s + *</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>8</td>
<td>CO₂ + s ⇄ CO₂s</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>9</td>
<td>2CO + O₂ → 2CO₂</td>
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</tr>
</tbody>
</table>

Ceria provides additional sites for oxygen chemisorption in the temperature range investigated, this effect being much more pronounced than on alumina (Jin et al., 1987a, 1987b, Serre et al., 1993b, Nunan et al., 1992a, Oh and Eickel, 1988). This is caused by the fact that ceria is prone to partial reduction, leading to an excess of metal atoms and a relatively large amount of oxygen vacancies (Krylov, 1970). Oxygen adsorbed on the ceria surface is readily available for reaction with CO adsorbed on noble metals, since the cerium-oxygen bond strength is optimal for oxidation reactions (Krylov, 1970).

At temperatures relevant to this study oxygen adsorbs at negatively charged oxygen surface vacancies forming O₂⁻ radical anions, reaction 5 in Table 4.8 (Gideoni and Steinberg, 1972, Che et al., 1973, Tong and Lunsford, 1991). Sass et al. (1986), proposed that the reaction with CO proceeds in two stages, reactions 6 and 7 in Table 4.8. The molecularly adsorbed oxygen species react with CO adsorbed on noble metal sites producing CO₂ and O⁻ anions. According to Kazanskii and coworkers (references in Sass et al., 1986), the reaction of CO with these atomic oxygen species is potentially faster than with O₂⁻ radical anions.

From the step change in isotopic composition from ¹⁶O₂ to ¹⁸O₂, see section 4.3.4, Figure 4.12, the maximum surface concentration of oxygen containing species leading to CO₂ amounted to 0.3 mol kg⁻¹. This amount is an order of magnitude larger than the total amount of noble metal present, hence, it is concluded that this species is oxygen, chemisorbed molecularly on ceria rather than on noble metal sites. Similar results were reported by Ouckaci et al. (1992). This explanation differs from Zafiris and Gorte (1993a), who explain the rate enhancement by ceria by assuming reverse spill-over of oxygen on noble metal particles. This does not seem reasonable, since in this study it was confirmed that the noble
metal particles are primarily covered by chemisorbed CO.

Since the CeO$_2$/Al$_2$O$_3$ support was not catalytically active, in agreement with Shido and Iwasawa (1993), the reaction most probably takes place at the noble metal/ceria interface. From Figure 4.12 it followed that CO$_2$ production proceeded via only one kinetically significant type of surface species. Reactions 6 and 7 in Table 4.8 are consistent with this observation if upon formation, O$_5$ species react instantaneously with CO*, rendering the O$_5$ species kinetically insignificant.

It follows from Figure 4.10 that CO$_2$ in the feed gas inhibits its net production rate. Reaction 8 in Table 4.8 has been incorporated since rate inhibition by CO$_2$ is assigned to blocking of oxygen chemisorption sites by CO$_2$ chemisorption on ceria, in agreement with Herz (1981), Jin et al. (1987b), Li et al. (1989a, 1989b), Barrault and Alouche (1990), Vonkeman (1990). Significant chemisorption of CO$_2$ on noble metal particles or on the Al$_2$O$_3$ surface does not seem likely under the experimental conditions (Chapter 3, Solymosi, 1991, Engel and Ertl, 1979, van Tol et al., 1993).

The relative importance of both mechanisms in Table 4.8 depends on the process conditions, particularly on the temperature and the feed composition. From Figure 4.6 it follows that the monofunctional reaction path becomes more important at increasing temperatures; at temperatures below 443 K CO$_2$ production is dominated by reaction path II. This transition of dominating reaction paths at different temperatures is also observed in the temperature dependence of the reaction, see Figure 4.11. The apparent activation energy below 450 K apparently corresponds to the bifunctional reaction path. At temperatures over 450 K the apparent activation energy does not reach the value of 110 kJ mol$^{-1}$, as expected from Chapter 3. This indicates that in the investigated temperature range, this apparent activation energy corresponds to both reaction paths.

The observed temperature dependence is in agreement with Sass et al. (1986), who attribute the increase in apparent activation energy at higher temperatures to an increasing importance of O$_2^-$ surface lattice anions. Although this is consistent with the generally observed tendency of adsorbed oxygen species to accept additional electrons at increasing temperatures (Bielanski and Haber, 1991), the results from this study indicate that the monofunctional reaction path has to be taken into account.

The influence of the feed composition on the contribution to CO$_2$ production of both mechanisms is illustrated by Table 4.7. The rate enhancement by ceria decreases when the CO to oxygen ratio in the reactor feed is decreased. This indicates the monofunctional reaction path becomes more important at increasingly oxidising conditions. This is due to the fact that low CO to oxygen ratios favour CO$_2$ production via this mechanism. In addition, due to the $n$-type semiconductor character of ceria, the concentration of oxygen chemisorption sites decreases at increasing oxygen partial pressure according to approximately $p_{O_2}^{-1/6}$ (Krylov, 1970, Breysse et al., 1972, Bielański and Haber, 1991).

From section 4.3.2 it follows that for the Rh/Al$_2$O$_3$ catalyst the turnover frequency is typically 3.5 times lower than for the Pt/Al$_2$O$_3$ catalyst at a temperature of 463 K, while
for the CeO$_2$ promoted catalyst the difference is much smaller. Assuming that CO oxidation over Rh/Al$_2$O$_3$ proceeds analogous to the reaction over Pt/Al$_2$O$_3$ (Chapter 3, Oh and Carpenter, 1986), the observed difference in turnover frequencies can be assigned to a larger activation energy for the reaction over Rh/Al$_2$O$_3$ than over Pt/Al$_2$O$_3$. The factor of 3.5 corresponds to a difference of 5 kJ mol$^{-1}$. In Chapter 3 it was concluded that the apparent activation energy for CO oxidation over a Pt/Al$_2$O$_3$ catalyst is equal to the desorption enthalpy of CO. The observed difference in activation energies indeed agrees with values reported for the difference in CO desorption enthalpy (Grenoble $et$ $al.$, 1981, Oh and Carpenter, 1986, Nieuwenhuys, 1983). The observation that the difference in turnover frequencies on Pt and Rh for ceria supported catalysts is smaller can be explained by reaction path II in Table 4.8. Since CO reacts with oxygen adsorbed on the ceria surface, the rate is no longer limited by oxygen chemisorption on noble metal particles and, hence, the stronger inhibition of the latter by CO on Rh is no longer as important. Similar results have been reported by Schlatter and Mitchell (1980), Engler $et$ $al.$ (1989), and Zaïris and Gorte (1993a).

### Effect of steam on CO oxidation

The presence of steam in dioxygen containing reaction mixtures was found to greatly enhance the CO$_2$ production rate over ceria promoted Pt and Pt/Rh catalysts, see Figures 4.1 to 4.3 and Table 4.10. For the Pt/Al$_2$O$_3$ and Pt/Rh/Al$_2$O$_3$ catalysts the effect was less pronounced while no significant effect of steam was observed for the Rh/CeO$_2$/Al$_2$O$_3$ and Rh/Al$_2$O$_3$. Furthermore, the water-gas shift reaction did not add significantly to the conversion of CO. The most striking result concerning the role of steam was obtained from steady state isotopic transient experiments in which a switch was made between $^{16}$O$_2$ and $^{18}$O$_2$, see Figures 4.13 to 4.15. It was demonstrated that CO$_2$ produced in the presence of dioxygen and steam contained oxygen atoms originating from steam rather than from dioxygen. This indicates that water acts as an important source of oxygen for reaction with CO despite the fact that no net disappearance of steam was observed. The latter can be explained by the observation that the production rate of CO$_2$ containing oxygen from water was equal to the production rate of water containing oxygen atoms from dioxygen. Hence, the majority of CO$_2$ production occurs according to the global equation:

$$2C^{16}O + ^{18}O_2 + 2H_2^{16}O \rightarrow 2C^{16}O_2 + 2H_2^{18}O$$  \hspace{1cm} (4.1)

Table 4.9 shows a reaction path to CO$_2$ that can account for the experimental observations. From the step changes $^{16}$O$_2$/$^{18}$O$_2$ in the absence and in the presence of steam it followed that the production rate of C$^{16}$O$^{18}$O was hardly affected by steam, see section 4.3.4. This implies that C$^{16}$O$^{18}$O is produced via the same reaction path, reaction path II in Table 4.8, both in the presence and in the absence of steam. Therefore, the reaction path expressing the influence of steam, reaction path III in Table 4.9, is considered to occur parallel to paths I and II presented in Table 4.8.
Water chemisorbs molecularly on metal oxides, reaction 9, (Rethwisch and Dumesic, 1986a, 1986b, Grenoble et al., 1981) and may dissociate to form surface OH-groups on so-called donor-acceptor pairs, reaction 10 (Krylov, 1970). Since the ceria surface contains a relatively large concentration of coordination-unsaturated metal atoms it is ranked among the strongest Lewis acids, stronger than alumina (Krylov, 1970). This facilitates water chemisorption on ceria (Sass et al., 1985, Padeste et al., 1993). Moreover, chemisorbed water will be more reactive on ceria than on alumina due to a weaker metal-oxygen bond strength in the former (Krylov, 1970, Rethwisch and Dumesic, 1986b). Significant water chemisorption on noble metals does not seem likely under the experimental conditions (Peng and Dawson, 1977, Nieuwenhuys, 1983, Heras and Viscido, 1988). This is substantiated by the observation that in the presence of relatively large amounts of steam no competitive chemisorption between CO and H$_2$O was observed.

In the preceding part of this discussion it was mentioned that the reaction of CO with atomic oxygen species, O$_8$, is potentially faster than with O$_{28}$ species, so the rate of CO$_2$ production is not limited by the former. If both OHs and O$_{28}$ are present, these more reactive O$_8$ species could be more readily formed according to reaction 11 in Table 4.9. Assuming this reaction is fast compared to reaction of CO* with O$_{28}$ seems reasonable, and this explains the observed rate enhancement by steam. It was observed that the production rate of C$^{16}$O$^{18}$O was hardly affected by steam addition. Hence, in the presence of steam little C$^{16}$O$^{18}$O is produced through reaction 11 from Table 4.9. This can be understood by assuming quasi-equilibrium for water chemisorption on ceria, reactions 9 and 10 in Table 4.9. Consequently, the probability of $^{18}$O leaving ceria as H$_2$$^{18}$O is large compared to the probability of $^{18}$O reacting with CO.

It follows from Figure 4.3 that the rate of CO$_2$ production over a Rh/CeO$_2$/Al$_2$O$_3$ catalyst is hardly affected by steam at a temperature of 463 K. This indicates that the CO$_2$ production rate over Rh/CeO$_2$/Al$_2$O$_3$ is limited by a different reaction than over ceria promoted Pt catalysts. Figure 4.3 also shows that, in the absence of steam, the CO$_2$ production rate over Rh/CeO$_2$/Al$_2$O$_3$ is independent of the oxygen partial pressure over the range of partial pressures applied. Hence, it is reasonable to assume that breaking the CO-Rh bond limits the CO$_2$ production rate rather than the rate of oxygen chemisorption and that the

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<td>10 H$_2$O$_8$ + Os ↔ 2O$_8$Hs</td>
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<td>11 2O$<em>8$Hs + O$</em>{28}$s → 3O$_{28}$ + H$_2$O</td>
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<td>7 CO* + Os ↔ CO$_2$ + s + *</td>
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$2$CO + O$_2$ → $2$CO$_2$
former is not oxygen assisted. This explains why rate enhancement by steam, reactions 9-11 in Table 4.9, is not observed. A similar result was reported by Muraki et al. (1991), who found that for Al₂O₃ supported Pt an Rh catalysts the rate enhancement by steam was much more pronounced for the former, while no significant water-gas shift was observed. Grenoble et al. (1981), studied the water-gas shift reaction on various noble metal/metal oxide catalysts and observed that supported Rh catalysts were typically less active than Pt catalysts by an order of magnitude and also attributed this to the larger CO-Rh bond strength compared to that of CO-Pt.

4.5 Conclusions

Enhancement of the CO₂ production rate by ceria can be attributed to both an increased fraction of exposed noble metal atoms on ceria containing catalysts and to higher turnover frequencies. The role of ceria can be described by a bifunctional reaction path that occurs parallel to the reaction path for CO oxidation on alumina supported noble metal catalysts. Essentially, in this second reaction path ceria provides oxygen chemisorption sites, resulting in less pronounced rate inhibition by CO.

Steam acts as an important source of oxygen for oxidation of CO if Pt is present but only in conjunction with dioxygen in the feed gas. In the presence of steam the behaviour of catalysts containing both Pt and Rh is mainly governed by platinum. The effect of steam can been described by a reaction path in which hydroxyl groups adsorbed on ceria react with molecularly adsorbed oxygen species, producing a higher steady state surface concentration of atomic oxygen species.

References

CHAPTER 4


-Nunan, J.G., Cohn, M.J., Donner, J.T., 'Effect of high temperature lean aging on the performance of Pt, Rh/ CeO$_2$ and rare earth/alkaline earth doped Pt/Rh/CeO$_2$ catalysts,' *Catalysis Today* 14, 77-90, 1992b.


EXPERIMENTAL SET-UP FOR THE INVESTIGATION OF FORCED CONCENTRATION CYCLING

5.1 Introduction

Typical automotive three-way catalysts are used to simultaneously convert CO, NO\textsubscript{x} and unburnt hydrocarbons to CO\textsubscript{2}, H\textsubscript{2}O and N\textsubscript{2} (Wei, 1975). In order to obtain sufficiently high conversions, the exhaust gas composition is controlled closely to the stoichiometric setpoint by means of a so-called Lambda sensor (Engh and Wallman, 1977, Taylor, 1984). By monitoring the oxygen concentration in the exhaust gas, this sensor supplies a signal that is used to manipulate the air-to-fuel ratio of the mixture injected into the engine.

The delay time in this feedback control loop causes the exhaust composition to oscillate around the stoichiometric setpoint with typical frequencies of 0.5 to 5 Hz, and amplitudes of 5 to 15 % of the time average concentrations (Canale et al., 1978). Table 5.1 shows typical exhaust compositions at three different air-to-fuel ratios (Taylor and Sinkevitch, 1983). It is known from theoretical studies that oscillatory feeding of chemical reactors may affect the time average conversion of reactants (Bailey and Horn, 1968, Bailey, 1977, Renken, 1984, Matros, 1989). Experimental studies have been dedicated to the influence of forced concentration cycling on the oxidation of CO (Cutlip, 1979, Schlatter et al., 1983, Taylor and...

Potential effects on the CO oxidation rate of forced concentration cycling can be understood by examination of some results discussed in Chapter 3. In Figure 5.1 the rate equation for CO oxidation, Equation 3.18, see sections 3.4 and 3.6, is plotted as a function of $P_{\text{CO}}$ at a fixed oxygen partial pressure of 2.2 kPa and a temperature of 483 K. The reactor operating at steady state with a CO partial pressure $p_1$ and a corresponding CO$_2$ production rate $R_1$, a step change in the CO partial pressure from $p_1$ to $p_2$ forces the reaction to reach a new CO$_2$ production rate $R_2$ corresponding to $p_2$. The time required for the system to reach the new CO$_2$ production rate is governed by the characteristic time, $\tau_0$, of the process. According to Figure 5.1, the concept of rate enhancement can be understood by modulating the partial pressure of CO between $p_1$ and $p_2$, with a period $T_m$ much larger than $\tau_0$. This type of periodic operation is known as quasi-steady state operation (Bailey, 1977, Matros, 1989). If the CO partial pressure were modulated in a square wave, the resulting time averaged CO$_2$ production rate would then be $R_{\text{av}} = \frac{1}{2}(R_1 + R_2)$, the time average CO partial pressure being equal to $P_{\text{av}} = \frac{1}{2}(p_1 + p_2)$. If the reactor is operating at steady state with $P_{\text{CO}} = P_{\text{av}}$, the corresponding steady state CO$_2$ production rate, $R_{\text{ss}}$, is lower than $R_{\text{av}}$. Quasi-steady state modulation can be interesting in reduction of automotive emissions, since in practice $P_{\text{av}}$ will be imposed on the catalytic converter by the engine. By slowly modulating $P_{\text{CO}}$ around $P_{\text{av}}$ CO conversion enhancement can be obtained. Note that the time average rate can never exceed the maximum rate attainable under steady state conditions: in this example $R_2$ is larger than $R_{\text{av}}$.

If the modulation period were much smaller than $\tau_0$, the reactor would be in sliding, or relaxed steady state operation (Bailey, 1977, Matros, 1989): the system cannot follow the perturbation and in the limiting case the CO oxidation rate assumes the value $R_{\text{ss}}$. Both quasi-steady state and relaxed steady state operation have in common that the behaviour of the system can be predicted if the steady state behaviour is known. The most intricate operation however, occurs when $T_m$ is comparable to $\tau_0$, and is called dynamic operation (Bailey, 1977, Matros, 1989). In order to predict the behaviour of the system in the dynamic regime the
transient behaviour has to be determined.

The regime of particular interest is the dynamic regime, since this is the only regime which potentially leads to rates that are higher than the maximum rate attainable under steady state conditions. In a modelling study, Lie et al., 1993, have shown that enhancement or deterioration of the CO oxidation rate are dependent on the operating conditions of the reactor, the cycling frequency, the duty fraction\(^1\) and the amplitude of the oscillation. In essence, rate enhancements were simulated under conditions where forced concentration cycling led to large changes in the CO and oxygen surface coverages, corresponding to temperatures below 600 K, a duty fraction of \(\frac{1}{2}\), meaning CO and \(\text{O}_2\) gas phase concentrations oscillating in counter-phase, and oscillation periods in the order of 1 to 10 seconds. These results, also applicable to CO oxidation by NO (Nievergeld, 1994) indicate that oscillatory feeding of exhaust catalysts has the potential of increasing the CO conversion at temperatures below light-off. This is important since at those temperatures the majority of noxious emissions occur, as stated in Chapter 1.

It can be shown that the shape of the concentration wave potentially affects the time averaged conversion of reactants (Feimer et al., 1982). Hence, in a study concerning the effect of forced concentration cycling on the time averaged conversion it has to be ensured that the shape of the concentration wave imposed on the reactor does not change significantly upon varying the cycling frequency.

In addition to the potential benefits on the conversion of forced concentration cycling, this type of experiments may also aid in kinetic parameter estimation and kinetic model discrimination (Bailey, 1977). This application of forced oscillations is known as the frequency response method. In Chapter 3 it was found that, under steady state conditions, the kinetic parameters of the reaction between CO and \(\text{O}_2\) appeared as lumped parameters, \textit{i.e.} estimation of the parameters of the individual elementary reaction steps was not possible. In general, transient kinetic experiments, and specifically frequency response experiments potentially allow estimation of parameters of individual processes since the characteristic times of these processes are generally different (Cutlip et al., 1983). Combination of both frequency response and steady state experiments remains indispensable, however, since numerous kinetic models proposed from transient experiments do not allow description of phenomenological steady state observations (Harold and Garske, 1991a, 1991b).

In order to enable intrinsic kinetic measurements from concentration cycling experiments a well defined concentration wave form should be imposed on the catalyst bed. The reactors most frequently encountered in literature are similar to the reactor designed for steady state experiments in this work; oscillations are generated by periodically switching between feed gases with different compositions significantly upstream of the reactor, while samples for chemical gas analysis are taken at a considerable distance downstream of the

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\(^1\)Oscillations take place between a high and a low value of the control variable, \textit{i.e.,} a reactant concentration. The duty fraction is defined as the part of the oscillation in which the control variable has the high value.
reactor. Due to backmixing of succeeding gas 'packages' upstream of the reactor, even at low oscillation frequencies the amplitude and the shape of the resulting input waveform are often a function of the frequency applied, as clarified in Fig. 5.2 (after: Weibel et al., 1991). Due to mixing in the reactor and in the gas analysis section it is difficult to assign changes in the waveform to either physical transport phenomena or to chemical kinetics, a problem that may have affected results reported by Taylor and Sinkevitch, 1983, and Cho, 1988. In addition, the gas analyses have to be performed very rapidly in order to allow monitoring of concentrations at higher oscillation frequencies.

The purpose of this work is designing a reactor and a means of chemical gas analysis that allow concentration cycling experiments at frequencies relevant to the practice of automotive three-way converters. The performance of the resulting experimental set-up is tested by forced concentration cycling using argon as an inert gas phase marker. Next, the feasibility of studying the effect of forced concentration cycling experiments on the time average CO conversion is evaluated, and the potential of forced concentration cycling experiments as a tool in kinetic modelling is shown.

5.2 Experimental

The experiments have been carried out using the set-up described in Chapter 2. However, the reactor section and the chemical gas analysis have been adapted as to fulfil the requirements for forced concentration cycling experiments. In addition, some features of the set-up specifically designed for this type of experiments have been left out of the discussion in Chapter 2, and will be clarified in this section.

Reactor section

In order to minimise the influence of significant backmixing of reactants and products on the square wave concentration cycles imposed on the reactor, a novel reactor has been designed, a longitudinal cross-section is depicted in Figure 5.3. The most important difference between this reactor and conventional types is that two feed streams are alternatingly fed to the reactor through two separate lines (1) instead of one. In the reactor inlet two chambers (2) have been machined in order to radially distribute each feed stream over three lines. Spring loaded valves, machined to precision and acting as one-way valves, have been placed downstream of the reactor inlet. The valves consist of sapphire beads (3), one for each line enter-
ing, which are retained by a centring ring (4). If not pressured, the sapphire beads are lifted by a flexible metal spring (5) mounted to the body of the inlet, thus closing the corresponding feed lines. The metal spring has been constructed of Duratherm, a Ti and Al containing Co/Ni/Cr alloy which retains its flexibility up to approximately 1000 K. The valve spring is retained by a sintered quartz plate (6) which also serves to enhance radial distribution of the inlet gas stream. Directly downstream of the sintered plate a mass spectrometer capillary is inserted into the first sample chamber (7) to allow real-time chemical analysis of the reactor feed entering the catalyst bed. The second sample chamber (9) is located immediately downstream of the catalyst bed (8), hence, the composition of the catalyst bed effluent can be monitored in time. The internal volumes of sample chambers and valve chamber are negligible under the operating conditions applied.

**Gas analysis section**

In Chapter 2 the procedure for on-line chemical gas analysis using a gas chromatograph has been described. During concentration cycling experiments, this means of analysis can be used to measure the time average flow rates of the reactor effluent. In order to allow real-time analysis of the gas composition at the reactor inlet and outlet during concentration cycling experiments, the quadrupole mass spectrometer described in Chapter 2 was used. Sample lines were located within two millimetres upstream and downstream of the catalyst bed, as shown in Figure 5.3, and were connected to a three-way valve connected to the mass spectrometer inlet. By switching the three-way valve, either the reactor feed or the effluent could be sampled. The time resolution of the mass spectrometer was enhanced by application of software and hardware originating from mass spectrometer systems used in breath analysis in a medical environment. This arrangement, provided by Fisons Instruments, allowed gas compositions to be determined at a frequency of typically 120/n Hz, where n denotes the number of atomic mass units (AMU) to be measured. This means that the composition of a mixture containing He, O₂, CO and CO₂ could be measured thirty times per second.

It was found that mass spectrometer analysis could not be used as a single quantitative
means of chemical analysis. In order to obtain quantitative measurements the mass spectrometer was calibrated daily as follows. A known gas mixture was passed through the reactor and the composition of the reactor effluent was simultaneously determined by GC and MS analysis. The mass spectrometer software only permitted determination of the normalised gas composition, meaning that the detector signals for each component were expressed as fractions of the total signal measured. The mass spectrometer signals were related to the flow rates measured with the GC by calibration factors, $f_i$, according to:

$$f_i I_i = \frac{F_i}{F_{tot}}$$

where $I_i$ denotes the mass spectrometer signal for component $i$.

Specific provisions for concentration cycling experiments

Referring to Figure 2.2, Figure 5.4 schematically shows the relevant details of the specific provisions for concentration cycling experiments in the experimental set-up. Square wave concentration cycles were generated by switching between two feed streams upstream of the reactor by passing the gas through a valve arrangement, consisting of four fast acting miniature two-way solenoid valves (Asco Angar 008, time to open or close: 3-5 ms). The valves were actuated by synchronised digital timers, the timer settings using 1 ms increments. This permitted either symmetrical or asymmetrical concentration cycling with frequencies between 0.05 and 20 Hz. By opening the valves two by two one feed stream was passed to the reactor while the other was by-passed to the exhaust. Due to the maximum operating temperature of 350 K specified for the solenoid valves, the feed gases had to be heated to the reaction temperature downstream of the solenoid valves.

Pressure changes in the reactor due to switching between the feed streams was prevented by carefully regulating the pressure in the feed lines upstream of the valve arrangement. The pressure control loop consists of: pressure controllers downstream of the reactor and in the by-pass line, a pressure indicating device located directly downstream of the reactor, a differential pressure indicator measuring the pressure difference directly upstream of the valve arrangement and two needle valves upstream.
of the differential pressure indicator. Preparing the set-up for forced concentration cycling experiments was carried out as follows. Two feed streams of equal molar flow rates, containing different mole fractions of argon in helium are generated as described in Chapter 2, and one stream is directed to the reactor while the other is by-passed. The desired reactor pressure is set by the pressure controller downstream of the reactor. The pressure controller in the by-pass line is manipulated until the pressures in both feed streams are equalised, as measured by the differential pressure indicator. The pressure controller in the by-pass line thus acts to simulate the resistances in the reactor line downstream of -and including- the valve arrangement. The needle valves were used as pressure reducers in order to prevent the feed section from responding to switching the valves. After setting one needle valve, the square wave of the argon tracer concentration, monitored by the mass spectrometer, was optimised by adjusting the second needle valve.

Catalyst pretreatment and line-out

The catalyst used was the same Pt/γ-Al₂O₃ catalyst described in Chapters 2 and 3, the reactor contained 0.20 g of catalyst diluted with 1.80 g α-Al₂O₃. The catalyst was pretreated as described in section 2.5, and lined-out as described in section 3.2.

Process conditions

Experiments described in this work were carried out at a temperature of 473 K and a pressure of 110 kPa. Concentration cycling using argon was performed by oscillating between two streams containing argon concentrations of 0.7 and 2.1 mol%, and a helium flow rate of 1.9 \( \times 10^{-3} \) mol s⁻¹. The oscillation frequency was varied between 0.1 and 5 Hz. A concentration cycling experiment under reaction conditions was carried out at 473 K by oscillating at a frequency of 1 Hz between a mixture containing 2 mol% CO and one containing 2 mol% O₂, the helium flow rate being 1.9 \( \times 10^{-3} \) mol s⁻¹.

5.3 Results and discussion

Argon concentration cycling

Figure 5.5 shows the argon inlet and outlet mole fractions as a function of time at oscillation frequencies of 0.5 Hz and 5 Hz. A symmetric square wave in the argon concentration was imposed and the gas analysis frequency amounted to 70 Hz. In the top graph the amplitude and the wave form at the reactor inlet and outlet are identical, indicating the reactor can be regarded as an ideal plug flow reactor at a frequency of 0.5 Hz. The time required to reach a steady mole fraction of argon after switching between the two feed streams amounted to 0.1 s.
From the bottom graph it follows that the oscillations are reproducible. The inlet and outlet mole fractions are within 10% of the argon mole fraction in the feed streams. At this frequency, the form of the concentration wave concentration tends to deviate from a square wave towards a sine wave. In the introduction of this Chapter it was mentioned that the shape of forced oscillations may affect the time averaged conversion. Therefore, an oscillation frequency of 5 Hz can be regarded as an upper limit in the study of the effect of forced concentration cycling on the time averaged conversion.

In kinetic modelling studies the shape of the concentration cycles as such is irrelevant as long as both the reactor inlet and outlet compositions can be measured with sufficient time resolution. It is, however, essential that the concentrations measured at the reactor outlet are not biased by physical transport phenomena in the reactor. At frequencies higher than 5 Hz the amplitude at the reactor outlet decreased due to significant back-mixing in the reactor. As a result, the set-up also allows transient kinetic experiments to be carried out at oscillation frequencies up to 5 Hz.

**CO and O\textsubscript{2} concentration cycling**

A forced concentration cycling experiment was carried out in which periodic switches at a frequency of 1 Hz were made between feed streams containing either oxygen or CO in helium. In Figure 5.6 and 5.7 the O\textsubscript{2} and CO concentrations, respectively, at the reactor inlet and outlet are shown as a function of time. The outlet signals clearly differ from the inlet signals, and on the basis of the argon concentration cycling experiment the difference can be assigned exclusively to kinetic phenomena.

In Figure 5.8 the outlet concentrations of CO, O\textsubscript{2} and CO\textsubscript{2} concentrations are shown. The time average CO conversion under these conditions amounts to 18%, whereas a steady state conversion of 3% was found using a mixture containing the time average CO and O\textsubscript{2} concentrations, 1 mol% each.

The enhancement of the time average CO conversion by forced oscillation cycling is caused by the fact that the steady state CO\textsubscript{2} production rate is inhibited by chemisorbed CO under the experimental conditions, as shown in Chapter 3. During the concentration cycles...
imposed in this experiment, the surface coverages oscillate between high and low values, and since the rate of $\text{CO}_2$ formation is proportional to the product of $\text{CO}$ and oxygen surface coverages, the rate is highest if both are of comparable magnitude. This result indicates that the set-up satisfies the requirements of well defined concentration wave forms and a high gas analysis time resolution, allowing to study the effect of $\text{CO}$ and $\text{O}_2$ concentration cycling on the time average $\text{CO}$ conversion.

In Figure 5.8 the onset of $\text{CO}_2$ production following a switch from $\text{CO}$ to oxygen and vice versa are markedly different. $\text{CO}_2$ production following the former switch lags the oxygen signal, whereas the opposite switch leads to $\text{CO}_2$ formation immediately. This can be assigned to the fact that oxygen cannot chemisorb at a substantial rate on a surface covered with $\text{CO}$, while $\text{CO}$ can chemisorb on an oxygen covered surface. Thus, modelling the $\text{CO}_2$ production rates as a function of time potentially allows discrimination between chemisorption characteristics of the reactants.

The kinetic merit of this experiment compared to steady state experiments is that in one oscillation period a large range of $\text{CO}/\text{O}_2$ ratios are imposed on the reactor, resulting in an abundance of kinetic information acquired in a single experiment. Moreover, changing the oscillation frequency was found to drastically change the shape of the $\text{CO}_2$ signal,
indicating the frequency response method has great potential in kinetic modelling of CO oxidation.

5.4 Conclusions

The set-up discussed in this chapter allows assessment of the influence of forced concentration cycling on the time average CO conversion at oscillation frequencies up to 5 Hz. The set-up satisfies the requirements of well defined concentration wave forms.

The set-up is also suited for transient kinetic experiments since the high gas analysis time resolution allows monitoring the reactor inlet and outlet concentrations. Transient kinetic experiments can be performed at frequencies up to 5 Hz, since at these frequencies the difference between reactor inlet and outlet concentrations can be fully ascribed to kinetic phenomena rather than to physical transport phenomena.

References


-Graham, W.R.C., Lynch, D.T., 'CO oxidation on Pt: Variable phasing of inputs during forced composition
EXPERIMENTAL SET-UP FOR THE INVESTIGATION OF FORCED CONCENTRATION CYCLING


SIMULATION OF AN INDUSTRIAL AUTOMOTIVE THREE-WAY CONVERTER

6.1 Introduction

Removal of harmful components from automotive exhaust is most commonly achieved by application of a so-called three way catalyst (Wei, 1975, Taylor, 1984), located in the exhaust pipe of a car. This type of catalysts, able to simultaneously oxidise CO and hydrocarbons and reduce nitrogen oxides, consists of a monolith reactor with several thousands of parallel channels coated with a washcoat layer. The washcoat consists of platinum, rhodium and/or palladium dispersed on an alumina support, which often contains considerable amounts of ceria and small amounts of additives. In a recent review, Cybulski and Moulijn (1994) discussed in detail the characteristics and applications of monolith reactors in heterogeneous catalysis.

In this Chapter, the steady-state oxidation of CO in a typical catalytic monolith reactor is simulated using the results of the kinetic study presented in Chapter 3. Both isothermal and non-isothermal reactor operation are addressed, and the influence of mass transfer limitation is evaluated. Since the majority of harmful automotive emissions occur after a cold start of the engine, exhaust gas temperatures below 600 K were chosen in the simulations.

The advantage of this approach of including an intrinsic kinetic rate equation into a physical reactor model is that it can be applied to a virtually unlimited range of reactor geometries, provided correlations for physical transport phenomena for these geometries are available. Furthermore, since physical and chemical behaviour of the reactor are separated in this method, more reliable models result as compared to modelling based on kinetic models derived under ill-defined reaction conditions, as often is the case (Schweich, 1994).
6.2 Model equations

Assumptions

For the development of the mathematical model several assumptions were made. The mass flows were assumed to be identical through each channel, despite the fact that the radial velocity profile in the exhaust pipe causes the mass flow in the outer channels to be lower than in the inner channels (Howitt and Sekella, 1974, Zygourakis, 1989). The flow in the channels is laminar since $Re$ is typically between 50 and 200. Entrance effects were neglected since the hydrodynamic entrance length is only a small fraction of the reactor length, typically 4% for $L = 0.15$ m, $d_b = 10^{-3}$ m and $Re = 100$ (Sherony and Solbrig, 1970). Only axial gradients of concentrations, temperature and gas velocity were considered. Radial concentration, temperature and velocity profiles were approximated by application of the asymptotic Sherwood and Nusselt numbers, $Sh = Nu = 3.66$, for fully developed flow in a circular channel with constant wall temperature (Shah and London, 1978). The reactor was considered adiabatic, which is reasonable since a real three-way converter is well insulated in order to enhance heating-up after a cold start of the engine. The heat conductivity of the solid was not taken into account, since there exists sufficient evidence that this is only relevant in non-steady state studies (Young and Finlayson 1976a, 1976b, Votruba et al., 1975, Kress et al., 1980). Diffusion coefficients were calculated according to the Füller-Schettler-Giddings correlation referred to in Chapter 2, Appendix 1. Pore diffusion limitation was neglected since the washcoat thickness is typically 25 µm. The Weisz modulus, see Equation 2.8, was calculated to be 0.14 based on a $CO_2$ production rate of $20$ mol $m_R^{-3}s^{-1}$, a diffusivity of $10^{-6}$ $m^2s^{-1}$ and a gas concentration near the catalyst surface of 0.01 mol $m^{-3}$.

Rate equation

The kinetic rate equation derived in Chapter 3, Eq. 3.18, was used in combination with the lumped kinetic parameters $A^{global}$ and $E_a^{global}$ described in Table 3.5, leading to:

$$R_w = A^{global} \exp \left(\frac{-E_a^{global}}{RT}\right) \frac{P_{O_2}}{P_{CO}} L_t$$

(6.1)

where $R_w$ denotes the specific production rate of $CO_2$ in units of $mol_{CO} kg_{washcoat}^{-1}s^{-1}$. From stoichiometry the following relation holds:

$$R_w = -R_{w,CO} = -2 R_{w,O_2}$$

(6.2)

The value of the kinetic parameters collected from Table 3.5 are listed in Table 6.1. The validity of this model was experimentally determined at an initial molar CO to oxygen ratio between 0.05 and 8 in a differential reactor. This implies that the model can be applied at
least in the range $0.05 \leq \frac{p_{CO}}{p_{O_2}} \leq 8$, were $loc$ denotes the local ratio of partial pressures in the pores of the washcoat of the monolith channel. Considering the rate equation it is clear that the situation of high CO conversion levels in stoichiometric or net oxidising mixtures cannot be described by Eq. 6.1, since the predicted CO$_2$ production rate would approach infinity. This is caused by the fact that in developing the kinetic model leading to Eq. 6.1 the molecular chemisorption of oxygen was considered rate-determining, see Chapter 3. This assumption obviously does not hold if the CO to oxygen ratio drops below a certain minimum value, as beyond that value another reaction step will be rate-determining. Hence, simulations concerning CO conversion in lean exhaust may be too optimistic.

**Reactor model**

The reactor model consists of a set of continuity equations for the reactants and, in case of non-isothermal operation, enthalpy balances in two phases: the bulk gas phase and the gas phase in the pores of the washcoat. No continuity equation for the catalytic surface is required since in development of the catalytic rate equation the concentrations of surface species have been eliminated, see section 3.4. The dependent variables were expressed as $C/\rho_f$ since Bos and Westerterp (1991) showed that neglecting density variations in tubular reactors may cause large errors.

Since the reaction is stoichiometrically single, continuity equations for one component, e.g. CO, are sufficient to calculate the concentration profiles, since the concentration of the other components, O$_2$ and CO$_2$ can be calculated from stoichiometry. The continuity equation for CO in the bulk gas phase is given by:

$$ \phi_m \frac{d}{dx} \left[ \frac{C_{f,CO}}{\rho_f} \right] + k_f a_v (C_{f,CO} - C_{s,CO}) = 0 \quad (6.3) $$

The enthalpy balance for the gas phase is given by:

$$ \phi_m \frac{C_{p,f}}{\rho_f} \frac{dT_f}{dx} + \alpha a_v (T_f - T_s) = 0 \quad (6.4) $$

The continuity equation for CO in the pores of the washcoat is given by:

$$ k_f a_v (C_{f,CO} - C_{s,CO}) + R_{v,i} = 0 \quad (6.5) $$

The corresponding enthalpy balance is given by Eq. 6.6:

$$ \alpha a_v (T_f - T_s) + R_v \Delta H_{f,CO_2} = 0 \quad (6.6) $$

The initial conditions for the continuity equations and the enthalpy balance which hold at $x = 0$ are:

$$ T_f = T_{f,0} \quad (6.7) $$
\[
\frac{C_{\text{f,CO}}}{\rho_f} = \frac{C_{\text{f,CO}}^0}{\rho_f} \quad \text{(6.8)}
\]

In Eqs. 6.5 and 6.6 \( R_{\text{v,i}} \) can be expressed in terms of \( R_{\text{w,i}} \) according to:

\[
R_{\text{v,i}} = R_{\text{w,i}} \frac{V_w}{V_r} \quad \text{(6.9)}
\]

The washcoat to reactor volume ratio can be calculated according to (Lie, 1992):

\[
\frac{V_w}{V_r} = 4 \varepsilon_R \frac{d_w}{d_b} \quad \text{(6.10)}
\]

In Eq. 6.9 the washcoat density, \( \rho_w \), has been taken as the density of the catalyst powder as received from Degussa rather than the density of the catalyst pellets used in the kinetic study. This choice is substantiated by the washcoating procedure usually applied, where the monolith is brought into contact with a slurry of fine powder support material (Cybulski and Moulijn, 1994).

The reactor parameter values used in this study are listed in Table 6.1, and have been taken from Lie et al., 1993.

### Table 6.1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>( 2.4 \times 10^3 )</td>
</tr>
<tr>
<td>( A_s )</td>
<td>( 6.0 \times 10^3 )</td>
</tr>
<tr>
<td>( \alpha_b )</td>
<td>( 1.0 \times 10^3 )</td>
</tr>
<tr>
<td>( d_w )</td>
<td>( 2.5 \times 10^{-5} )</td>
</tr>
<tr>
<td>( k_{\text{f,CO}} ) (500 K)</td>
<td>0.187</td>
</tr>
<tr>
<td>( k_{\text{f,O}_2} ) (500 K)</td>
<td>0.186</td>
</tr>
<tr>
<td>( L )</td>
<td>0.15</td>
</tr>
<tr>
<td>( Sh )</td>
<td>3.66</td>
</tr>
<tr>
<td>( Nu )</td>
<td>3.66</td>
</tr>
<tr>
<td>( \varepsilon_R )</td>
<td>0.60</td>
</tr>
<tr>
<td>( \rho_w )</td>
<td>510</td>
</tr>
<tr>
<td>( \rho_f ) (500 K)</td>
<td>0.68</td>
</tr>
<tr>
<td>( \gamma_{\text{global}} )</td>
<td>( 5.40 \times 10^{11} )</td>
</tr>
<tr>
<td>( E_{\text{global}} )</td>
<td>( 1.12 \times 10^5 )</td>
</tr>
<tr>
<td>( L_i )</td>
<td>( 1.12 \times 10^2 )</td>
</tr>
</tbody>
</table>

The solution procedure

The set of equations to be solved consists of two ordinary non-linear differential equations, Eqs. 6.3 and 6.4, coupled to two non-linear algebraic equations, Eqs. 6.5 and 6.6. The ordinary differential equations were numerically integrated along the reactor coordinate using the routine D02EBF from the NAG library (NAG, 1991). This routine integrates stiff ordinary differential equations using Euler's backward differentiation formulae with variable order and variable step size. The set of algebraic equations were solved numerically using the routine C05NBF from the NAG library (NAG, 1991), implementing Newton's back substitution formulae.

The set of non-linear algebraic equations can be solved analytically for the reactant concentrations and temperature in the pores of the monolith. However, this may lead to multiple solutions due to the non-linear character of the equations. These solutions can even be negative or complex, depending on the feed gas composition, mass flow rate and temperature. Similar problems using these so-called 'lumped parameter models' have been
reported by Young and Finlayson, 1976. In numerical solution of these equations the result may depend on the starting values for the variables (Heek et al., 1976). Since these initial values can be accurately supplied, i.e., $C_{s,i} = C_{r,i}$ and $T_{s} = T_{f}$ at the entrance of the reactor, the correct solution can always be determined numerically.

Calculations were performed on a DECStation 5000/100Series workstation, a typical computation required 5 seconds of CPU time.

6.3 Results and discussion

Isothermal versus non-isothermal model

Simulations were carried out in order to assess the effect of a temperature profile developing in the reactor. The feed gas mixture contained 0.6 mol% CO and 0.3 mol% $O_2$. The mass flow rate through the reactor amounted to $5 \times 10^{-3}$ kg s$^{-1}$, which is a typical exhaust gas flow rate from an idling 2 litre engine. In Figure 6.1 the axial concentration profiles in the reactor are shown as calculated at an engine exhaust gas temperature of 515 K. The conversions of CO and $O_2$ at the outlet of the reactor calculated with the isothermal model amounts to 33% whereas the non-isothermal model predicts a conversion of 99%. This considerable increase in conversion is due to the fact that the reaction lights-off in the non-isothermal reactor, resulting in an increasing oxidation rate as compared to the isothermal reactor. At an engine exhaust gas temperature of 500 K the conversions in the isothermal and non-isothermal reactor amounted to 15 and 21%, respectively, the smaller difference indicating the reaction did not light-off in the non-isothermal reactor at this reactor inlet temperature.

The axial temperature and rate profiles in the non-isothermal reactor corresponding to Figure 6.1 are shown in Figure 6.2. The axial temperature rise of the gas phase amounts to 60 K, which is close to the adiabatic temperature rise. The oxidation rate reaches a maximum of 5.2 mol m$^{-3}$ s$^{-1}$ close to the reactor outlet, followed by a rapid decrease in the last part of the reactor. Considering the kinetic rate equation this behaviour can only be explained for a stoichiometric mixture if significant mass transfer resistance occurs, so the reaction becomes stoichiometrically limited by a lack of oxygen in the pores of the washcoat. In the absence of mass transfer limitation the rate should increase continuously since the rate equation, Eq. 6.1, predicts a rate invariant with respect to conversion in stoichiometric mixtures. The situation occurring in such an instance is not covered by Eq. 6.1 as discussed in section 6.2. In the
isothermal case the oxidation rate was found to be uniform in the reactor. Since the feed composition was stoichiometric, this means the CO to oxygen molar ratio in the pores of the washcoat were uniform, indicating negligible mass transfer resistance under the conditions considered.

The results indicate that thermal effects have to be taken into account despite the highly diluted CO/O₂ mixtures used, so, in the remainder of this chapter the simulations pertain to the non-isothermal model, unless mentioned otherwise.

Effect of heat and mass transfer resistance

In the previous section it was concluded that mass transfer limitation affected the CO oxidation rate in a non-isothermal reactor at a mass flow rate of 5.0 \(10^{-5}\) kg s\(^{-1}\) and a reactor inlet temperature of 515 K. Figure 6.3 shows the influence of heat and mass transfer resistance on the CO and O₂ conversions calculated for 2.5 \(10^{-2}\) kg s\(^{-1}\) of exhaust gas containing the same stoichiometric mixture described in the previous section at a reactor inlet temperature of 550 K. Transfer limitations enhance the conversion, amounting to 97% as compared to 80% in the absence of significant limitations. From Figure 6.2 it was concluded that mass transfer limitation caused the oxidation rate to decrease using a stoichiometric mixture, hence, the increase in oxidation rate must be caused by heat transfer limitation. This leads to a higher temperature in the washcoat since the heat produced by reaction cannot be transferred to the gas-phase at a sufficient rate. Figure 6.4 shows the temperature profiles in the bulk gas-phase and in the washcoat corresponding to Figure 6.3. Indeed, a temperature difference between the gas-phase and the washcoat exists, amounting from 1.7 K at the reactor entrance and going through a maximum of 14 K.

In Figure 6.5 the rate profiles calculated with and without transfer resistance are shown. The higher rates caused by heat transfer resistance are counteracted by mass transfer resistance, as was expected on the basis of Figure 6.2.
Effect of gas composition

In order to gain insight into the CO conversion at low temperature simulations were performed in which the initial CO and oxygen concentrations were varied at a constant exhaust temperature of 503 K and a mass flow rate of $1.0 \times 10^{-2}$ kg s$^{-1}$, see Figure 6.6. At low CO concentrations the conversion of CO increases more than linearly with the $O_2$ concentration, due to a temperature profile in the reactor. Mass transfer limitations do not significantly affect $X_{CO}$ under these conditions. At $y_{CO} = 2.0\%$ and $y_{O_2} = 3.0\%$, corresponding to the highest conversion, the washcoat temperature at the outlet of the reactor amounts to 556 K, decreasing to 503 K when going to conditions with lower CO conversions.
Effect of Pt distribution

From the preceding results it can be concluded that at temperatures around 500 K the CO conversion rapidly increases with increasing temperature. In order to enhance the low temperature conversion without increasing the total amount of platinum per converter, non-uniform Pt loading may be beneficial, if Pt is deposited according to a degressive profile, i.e., a higher Pt loading at the reactor entrance, gradually decreasing towards the reactor outlet (Oh and Cavendish, 1982). Figure 6.8 shows the result of a simulation carried out in order to investigate this phenomenon using a mixture containing 0.6 vol% CO and 0.3 vol% O₂, a mass flow rate of 1.0 \(10^{-2}\) kg s⁻¹, at an inlet temperature of 520 K. The corresponding platinum loading, arbitrarily chosen to exponentially decrease from 1 w% at the reactor inlet, is shown in Figure 6.7; note the average Pt loading equals the loading used in the preceding simulations, i.e. 0.398 w%. The conversions in the non-uniformly loaded converter amounts to 49%, compared to 34% at uniform loading. From Figure 6.8 this can be explained by a higher initial CO oxidation rate, resulting in a higher temperature in the washcoat. With increasing reactor coordinate the rate decreases for the non-uniformly loaded catalyst due to a decreasing platinum loading. Overall, the influence of the degressive platinum profile is beneficial, a possible drawback may be that at higher temperatures the thermal stress in the monolith will increase due to a steeper temperature gradient.

Influence of secondary air supply

It is well known that most of the harmful automotive emissions occur in the first few minutes after a cold start of the engine (Rijkeboer, 1991). From engine dynamometer testing Laurikko (1989) reported maximum CO concentrations of 6 to over 10 vol% shortly after a cold start using a commercial 2 litre engine equipped with fuel injection and a three-way catalyst. These high concentrations were due to the enrichment circuit in the fuel injection system, probably in order to enhance
drivability with a cold engine. As a result the temperature in the converter was reported to rise to the normal operating temperature, amounting to 800 K without substantial CO oxidation occurring due to a lack of oxygen.

The amount of oxygen in the exhaust gas may be increased by adding air to the exhaust gas upstream of the converter, also known as secondary air supply. This technique has been used since the early eighties, as mentioned in Chapter 1, Table 1.1. Secondary air supply exhibits two interconnected advantages: CO emission shortly after a cold start is reduced while the conversion of relatively large amounts of CO enhances warming-up of the converter.

Figure 6.9 shows a simulation of the influence on the CO conversion of adding secondary air containing 20 vol\% O\(_2\) at 293 K. The resulting temperatures at the reactor inlet and outlet are also shown. The air was hypothetically added to a flow of 1.0 \(10^2\) kg s\(^{-1}\) of exhaust gas at a temperature of 557 K, containing 5 vol\% CO and 0.1 vol\% O\(_2\). Note that the mass flow rate of this exhaust gas is kept constant, hence, addition of air leads to a higher total mass flow rate. Initially, the conversion of CO increases from 0.5\% without addition of air to 7.4\% on adding 7.5 \(10^4\) kg s\(^{-1}\) of air, due to the presence of an increasing amount of oxygen at sufficiently high temperatures. Addition of air flows in excess of 7.5 \(10^4\) kg s\(^{-1}\) causes the CO conversion to decrease. This decrease is caused by a lower gas temperature, due to addition of larger amounts of cold air, at the reactor entrance. Addition of 3.0 \(10^3\) kg s\(^{-1}\) of air causes the gas temperature to drop to 504 K, which is, under the conditions, too low for the reaction to occur at a substantial rate, despite the fact that oxygen is present in excess.

The optimum secondary air flow rate increases with increasing exhaust gas temperature, since then a larger amount of cold air is required to extinguish the reaction.

It may be concluded that secondary air supply may increase the conversion of CO, the optimum amount of air added being a function of exhaust gas temperature, flow rate and composition. Hence, in order to fully appreciate the beneficial effect of secondary air supply the admission should be a control variable in the fuel injection system.
6.4 Conclusions

It has been demonstrated that including an intrinsic kinetic rate equation into a physical reactor model allows simulation and optimisation of automotive exhaust catalysts. It should be noted, however, that the validity of the kinetic model should be kept in mind, i.e., extrapolation of model results beyond the range of experimental conditions under which the model has been developed should be carried out with caution.

Even at low temperatures and using highly diluted CO/O\textsubscript{2} mixtures, non-isothermal effects of CO oxidation should be taken into account since considerable axial temperature profiles develop under these conditions. Furthermore, using the kinetic rate equation, Eq. 3.20, a maximum was found in the CO\textsubscript{2} production rate in a stoichiometric exhaust gas, the rate decreasing due to significant mass transfer limitation of oxygen from the gas phase to the pores of the washcoat at high oxygen conversion levels. This indicates that mass transfer limitation has to be taken into account if the reactor is simulated as a non-isothermal reactor. In an isothermal reactor the effect of mass transfer on the CO\textsubscript{2} production rate was less pronounced.

Heat transfer limitation may lead to a higher CO conversion because the heat produced during reaction in the washcoat cannot be transferred to the gas phase at a sufficiently high rate. This leads to an enhancement of the CO\textsubscript{2} production rate in the washcoat. In a stoichiometric mixture the beneficial effect of heat transfer limitation prevails over the detrimental effect of mass transfer limitation.

Considering the importance of heat generation in the reactor at exhaust gas temperatures around 500 K, Pt loading according to a degressive profile has been shown to be advantageous for CO conversion without increasing the total amount of Pt per converter. At the reactor inlet the CO\textsubscript{2} production rate increases because of the larger amount of Pt present, causing a steeper temperature profile in the reactor as compared to a uniformly loaded catalyst. Therefore, the reaction proceeds at a sufficiently high rate as a function of the axial reactor coordinate, despite the fact that the Pt loading decreases accordingly.

Since car driveability requires rather enriched air/fuel mixtures shortly after a cold start, a lack of oxygen exists in the exhaust gas under those conditions, causing the majority of CO emission to occur in the first few minutes after a cold start. Secondary air supply can be helpful in reducing these emissions if the amount of air added is carefully adjusted to the exhaust gas temperature, mass flow rate and composition. If too much air is added, this may cause the reaction to extinguish since the exhaust gas temperature falls if cold air is added.
SIMULATION OF AN INDUSTRIAL AUTOMOTIVE THREE-WAY CONVERTER

References

-Schweich, D., 'Laboratory data for three-way catalytic converter modeling,' Preprints of the Third International Congress on Catalysis and Automotive Pollution Control (CapoC3), 29-42, 1994.
GENERAL CONCLUSIONS

The work in this thesis was focused on the catalytic oxidation of carbon monoxide using supported platinum catalysts. Experiments were carried out under well-defined reaction conditions, chosen to be relevant with respect to the practical use of automotive three-way catalysts.

Several elementary step reaction paths were developed for CO oxidation by O\textsubscript{2} using a Pt/γ-Al\textsubscript{2}O\textsubscript{3} catalyst under steady-state conditions. Statistical testing of these models showed that only models based on the assumption that carbon monoxide chemisorption on platinum sites is at quasi-equilibrium were able to describe the experimental data with statistical significance. However, physical interpretation of the kinetic parameters of the models learned that only the model in which irreversible molecular chemisorption of oxygen was considered to be rate determining, featured the temperature dependence that was observed experimentally. In this model, once chemisorbed molecularly, oxygen dissociates to produce oxygen adatoms on platinum surface sites, which react with CO, both steps being potentially faster than oxygen chemisorption. Using this model, no discrimination can be made between reaction of oxygen atoms with CO chemisorbed on Pt or with CO from the gas phase, since the reaction step is kinetically insignificant under the conditions investigated.

Steam was found to enhance the CO\textsubscript{2} production rate using the Pt/γ-Al\textsubscript{2}O\textsubscript{3} catalyst, the effect being largest at low steam partial pressures, while the water-gas shift was insignificant under the conditions investigated. The experimental results could be described with statistical significance using the same rate equation as in the absence of steam, but with different kinetic parameters. The results were explained by assuming a bifunctional reaction path in which steam is activated by Al\textsubscript{2}O\textsubscript{3}.

Using a commercially available Pt/Rh/CeO\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3} catalyst it was found that the
intrinsic production rate of CO$_2$ was larger than in the absence of CeO$_2$. A bifunctional reaction path was developed to explain the results. In this reaction path oxygen chemisorbs molecularly on the CeO$_2$ surface while CO chemisorbs on the noble metal surface. Strong experimental indications were found for this path to occur parallel to the monofunctional reaction path that was selected for the reaction on the Pt/Al$_2$O$_3$ catalyst. Hence, the contribution of both reaction paths is a function of the process conditions.

The influence of steam on the CO oxidation over the commercial catalyst was found to be more pronounced than on the ceria-free catalyst. Isotope tracing experiments showed that, although no net production of H$_2$O occurred, steam is directly involved in the formation of CO$_2$. A reaction path was proposed in which water chemisorption on the CeO$_2$ surface is in quasi-equilibrium. Hydroxyl groups on CeO$_2$ react with molecularly chemisorbed oxygen to produce more reactive atomic oxygen species, hence enhancing the CO$_2$ production rate.

In order to study the effects of forced concentration cycling, a novel set-up was built. Using the Pt/γ-Al$_2$O$_3$ catalyst it was shown that forced concentration cycling may improve the CO conversion compared to the steady-state conversion. Moreover, it was concluded that this set-up could be used to perform transient kinetic studies on CO oxidation in order to obtain more kinetic information about the elementary reaction steps.

The behaviour of an industrial automotive three-way catalyst was simulated mathematically under conditions relevant to the warm-up period. The mathematical model consisted of the intrinsic kinetic rate equation derived for CO oxidation using the Pt/γ-Al$_2$O$_3$ catalyst and a reactor model containing physical transport parameters. It was demonstrated that an intrinsic kinetic model derived from experimental data acquired under well defined reaction conditions can be successfully used to optimise catalyst properties and dimensions.
CURRICULUM VITAE


DANKWOORD

In tegenstelling tot wat de omslag doet vermoeden, is dit proefschrift niet het werk van één persoon. Ik wil dan ook iedereen die aan de totstandkoming hiervan heeft meegewerkt hartelijk danken.
1. Omdat Serre et al. geen melding maken van enkele essentiële experimentele omstandigheden, is het door hen voorgestelde reactiemechanisme voor de oxydatie van CO op een Pt/CeO₂/Al₂O₃ katalysator speculatief.


2. De door Schwartz et al. als elementaire reactiestap voorgestelde dissociatieve chemisorptie van zuurstof op edelmetaaloppervlakken is niet te rijmen met de door hen voorgestelde reactiesnelheidsvergelijking voor de oxydatie van CO.

Hoofdstuk 3 van dit proefschrift;

3. De verhoging van de CO₂ produktiesnelheid door stoom tijdens de oxydatie van CO met O₂ op een met ceria gepromoteerde Pt/γ-Al₂O₃ katalysator kan bij temperaturen tot 600 K niet worden verklaard door het optreden van de water-gasshiftreactie.

Hoofdstuk 4 van dit proefschrift.

4. De treffende fenomenologische overeenkomst tussen de invloed van water op de heterogeen gekatalyseerde oxydatie van CO en de homogeen gekatalyseerde oxydatie van ethanol leidt tot het vermoeden dat eerstgenoemde verloopt via formiaatintermediairen.

Hoofdstuk 4 van dit proefschrift;
5. Het bestuderen van de invloed van oscillerende voedingssamenstelling op chemische kinetiek in de door Weibel et al. gebruikte proefopstelling geeft aanleiding tot de welhaast filosofische vraag: 'is een frequentie van 1 Hz nu hoger of lager dan een van 0.075 Hz?'.

Hoofdstuk 5 van dit proefschrift;

6. LPG als brandstof voor auto's heeft voor het milieu in Nederland als potentieel nadeel dat door de lage prijs van deze brandstof een belangrijke drijvende kracht voor zuinig rijden ontbreekt.

7. Voor onderzoeksapparatuur geldt: 't is niet omdat je iets hebt dat het werkt.


9. Gevoelige mensen worden vaak atheïst op ethische gronden.

Andreas Burnier, geciteerd in: Beukel, A. van den, 'Met andere ogen; over wetenschap en het zoeken naar zin,' Ten Have, Baarn, 1994.

10. De hysterie rondom het feit dat voor ontvangst van het nieuwe Sportkanaal twee gulden per maand moet worden betaald staat in schril contrast tot de gelatenheid waarmee Nederlanders in het algemeen verlies van koopkracht accepteren.

11. Reclamespotjes waarin de fabrikant zijn produkt 'vernieuwde X-Ultra' vergelijkt met zijn klaarblijkelijk iets minder verfijnde voorganger 'X-Super', impliceren dat men al tijden door de fabrikant van 'X' is bedonderd.