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Kinetic modelling of the dynamic behaviour of an automotive three-way catalyst under cold-start conditions

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SUMMARY

During the cold-start period of an automotive exhaust gas converter, the slow kinetics of the catalytic reactions lead to emission of harmful gases into the environment. In order to optimise the operation of the current converter, detailed kinetic knowledge is necessary. The dynamic nature of the converter operation requires the use of transient kinetic procedures to develop accurate kinetic models. Such models can be used to create a model predictive controller, which creates optimal process conditions in the converter under all circumstances. Elementary step models are generally more accurate than empirical models and give more insight into the catalytic processes. Current literature in this respect mainly focuses on single reactions and on steady state conditions. Models using complex exhaust gases are mostly based on empirical kinetics. This thesis presents an elementary step model, obtained from transient experiments over one commercial Pt/Rh/CeO$_2$/γ-Al$_2$O$_3$ three-way catalyst for an exhaust gas, consisting of hydrocarbons, carbon monoxide, and nitric oxides.

The experimental set-up consists of a catalytic fixed bed reactor with two separate gas inlets, which enable fast switching between rich and lean reactor feeds. Special attention is paid to the analysis system, where a high-resolution magnetic sector mass spectrometer has been used. This instrument allows separation of the isobaric masses of C$_2$H$_4$, CO and N$_2$ as well as CO$_2$ and N$_2$O, which are separately monitored in real time. Therefore, individual rate parameters for reactions of all gaseous compounds could be determined. A dedicated hardware set-up as well as software were developed for the successful application of the instrument.

The transient kinetics of ethylene oxidation by oxygen over the Pt/Rh/CeO$_2$/γ-Al$_2$O$_3$ three-way catalyst were modelled. Ethylene was chosen as a model component for those hydrocarbons in an exhaust gas, which can be oxidised rather easily, such as olefins and aromatics. Moreover, ethylene is present in quite large quantities in an engine exhaust gas. Experiments were carried out in the fixed-bed reactor, while alternating between feeds of ethylene and oxygen with frequencies up to 1/4 Hz. The experimental conditions resemble the cold-start period of an Otto engine in a car. Two types of adsorbed ethylene species seem to exist. A selective catalyst deactivation for oxygen adsorption, due to deposition of carbonaceous species, was found. A kinetic model was developed, based on elementary reaction steps, that allows to describe the experiments quantitatively. Furthermore, this model was combined with the published model for transient carbon monoxide oxidation over the same catalyst, which enables to predict the results of simultaneous ethylene and carbon monoxide oxidation. Both components react in rather distinct zones, ethylene being converted only when carbon monoxide oxidation is almost complete. LEIS experiments have both qualitatively and quantitatively verified the catalyst deactivation by deposition of
carbonaceous species from either ethylene or acetylene; a complete restoration of the Pt surface was achieved after exposure of the catalyst to atomic oxygen.

The steady state and transient kinetics of acetylene conversion by oxygen over the Pt/Rh/CeO\textsubscript{2}/\gamma-Al\textsubscript{2}O\textsubscript{3} catalyst have been modelled. Acetylene is chosen because of its relative abundance immediately after the start of the engine, and because of its inhibiting behaviour towards the catalyst light-off. Experiments to determine rate parameters for the models were carried out in the fixed-bed reactor. The experimental conditions resemble the cold-start period of an Otto engine. Steady state experiments show that acetylene inhibits both adsorption of itself and of oxygen. CO is the primary reaction product of acetylene oxidation. For the transient experiments, alternate feeding of acetylene and oxygen has been applied at frequencies up to 1/6 Hz. Two types of adsorbed acetylene species seem to exist. A selective catalyst deactivation for oxygen adsorption, due to deposition of carbonaceous deposits, was found, as in the case of ethylene oxidation. Ceria proved to have a significant influence on the acetylene oxidation. Kinetic models were developed for the steady state and transient conversion of acetylene to carbon monoxide, based on elementary reaction steps. The transient model consists of the same reaction steps as the steady state model plus additional steps, required to explain phenomena not observed under steady state conditions. These models were both combined with the published kinetics for transient carbon monoxide oxidation over the same catalyst, in order to describe the total oxidation of acetylene quantitatively. The steady state model gives a reasonable prediction of the measurements. The combined transient model provides a good description of the transient experiments on simultaneous acetylene and carbon monoxide oxidation. During a transient, both acetylene and carbon monoxide react mainly in a front moving through the reactor, while carbon monoxide hardly influences the acetylene oxidation.

The reduction of NO by CO in absence and presence of O\textsubscript{2} has been investigated by transient experiments at automotive cold-start conditions over commercial Pt/Rh/CeO\textsubscript{2}/\gamma-Al\textsubscript{2}O\textsubscript{3}, and derived model catalysts. The high resolution magnetic sector mass spectrometer was used for distinction between CO and N\textsubscript{2} and between CO\textsubscript{2} and N\textsubscript{2}O. Mechanisms were compared for the different catalyst formulations. A kinetic scheme of elementary reaction steps is proposed, which highlights the various contributions of the catalyst constituents. The kinetic rate coefficients have been determined via regression of the transient experiments. The kinetic model quantifies storage and release of O\textsubscript{2} and NO in ceria during lean and rich half-cycles.

The complete kinetic model for the commercial automotive exhaust gas catalyst on the bases of elementary reaction steps has been developed by adding the aforementioned models together. Hence, this model involves the oxidation of CO, C\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4} as well as reactions of NO to NO\textsubscript{2}, N\textsubscript{2}O and N\textsubscript{2}. The kinetic model is capable of adequately predicting catalyst surface coverages and gas phase concentrations in time and along the axial reactor axis of transient cold-start experiments, performed with feed-cycling synthetic exhaust gases in a laboratory fixed-bed reactor over a Pt/Rh/CeO\textsubscript{2}/\gamma-Al\textsubscript{2}O\textsubscript{3} catalyst, where one feed contains only rich components and the other feed contains only lean components. The model shows explicitly the importance of the influence of ceria, like O\textsubscript{2} and NO storage, as well as bifunctional reactions between the noble metal and the ceria surface. These latter reactions involve CO, C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{2} oxidation, as well as ceria assisted NO dissociation. The effect of high concentrations of water and carbon dioxide was investigated qualitatively. Carbon dioxide inhibits the catalyst, probably by reversible adsorption on ceria. Water also absorbs on ceria, where it inhibits adsorption of NO, and strongly enhances the rates of the bifunctional path reactions. The oxidation of CO is effected most.
Verification of the model was performed by comparing model predictions with experiments, performed at conditions closer to real exhaust gas catalysis. This involves a synthetic gas experiment with reactor feeds around $\lambda = 1$ with a frequency of 1 Hz, and an experiment under lean-burn conditions. The activity of the catalyst under the conditions, where oxygen is present in both reactor feeds, is lower than predicted. This may be caused by a reversible over-oxidation of the catalyst or by segregation of Pt and Rh on the catalyst surface. Since such phenomena are not included in the model, it is not able to give adequate predictions for all components.

Engine-bench tests (stoichiometric and lean light-off, as well as a $\lambda$ sweep test) have been performed in order to investigate whether the model is able to predict the catalyst behavior when exposed to real engine exhausts. The model predictions for the stoichiometric light-off test are reasonable, but for the lean light-off test and the sweep test, they are not. The predicted conversions of most components are too low, indicating that the rate enhancing effect of water, as well as not included reactions like water-gas-shift and steam-reforming, may be important after the light-off.

The presented model is able to adequately predict transient synthetic gas experiments, where one feed contains only rich components, and the other feed only lean components. For the accurate prediction of conversions of real engine exhaust gases and of synthetic gases, where oxygen is continuously present, the model needs to be extended.
SAMENVATTING

Tijdens de koude-start periode van een benzinemotor leidt de trage reactiekinetiek van de uitlaatgaskatalysator tot de emissie van schadelijke componenten in het milieu. Om de werking van de huidige katalysator te optimaliseren, is gedetailleerde informatie over de reactiekinetiek noodzakelijk. De dynamische manier van het bedrijven van de uitlaatkatalysator vereist het gebruik van transiënt kinetische methoden voor de ontwikkeling van nauwkeurige modellen. Zulke modellen kunnen worden gebruikt voor de ontwikkeling van model gestuurde regelaars, die optimale condities creëren voor alle mogelijke omstandigheden. Modellen, gebaseerd op elementaire stappen, zijn in het algemeen nauwkeuriger dan empirische modellen en geven een beter inzicht in de katalytische processen. De huidige literatuur richt zich voornamelijk op enkelvoudige reacties en op de stationaire toestand. Modellen, gebaseerd op uitgebreidere uitlaatgasmengsels, zijn voornamelijk gebaseerd op empirische modellen. Dit proefschrift gaat over de ontwikkeling van een elementaire stappen model, verkregen uit transiënte experimenten, welke zijn uitgevoerd over een commercieel verkrijgbare Pt/Rh/CeO₂/γ-Al₂O₃ driewegkatalysator. Het model omvat de oxidaties van koolmonoxide en koolwaterstoffen en de reductie van stikstofoxide.

De experimentele opstelling bestaat uit een katalytische gepakt bed reactor met twee afzonderlijke voedingssystemen, die het mogelijk maken om rijke en arme gasmengsels alternerend aan de reactor te voeden. Speciale aandacht is besteed aan de gas analyse, waarbij gebruik is gemaakt van een magnetische sector massaspectrometer, welke met een hoge massaresolutie kan meten. Dit houdt in dat zowel de isobare massa's van etheen, koolmonoxide en stikstof als die van kooldioxide en lachgas apart kunnen worden gevolgd in de tijd. Specifiek ontwikkelde apparatuur en programmatuur was noodzakelijk voor de succesvolle toepassing van deze massaspectrometer.

De transiënte kinetiek van etheenoxidatie door zuurstof over de Pt/Rh/CeO₂/γ-Al₂O₃ katalysator is gemodelleerd. Etheen is gekozen als modelcomponent voor die koolwaterstoffen in een autouitlaatgas, welke redelijk eenvoudig zijn te oxideren, zoals alkenen en aromaten. Verder is etheen zelf ook in tamelijk grote hoeveelheden aanwezig in een autouitlaatgas. Experimenten zijn uitgevoerd in de gepakt bed reactor, waarbij voedingen met etheen en zuurstof zijn gealterneerd met frequenties tot ¼ Hz. De experimentele condities komen overeen met de koude-start van een Otto motor in een auto. Er blijken twee typen etheen op het katalysatoroppervlak te bestaan. Een selectieve deactivering voor zuurstofadsorptie is gevonden. Deze is te wijten aan de afzetting van kool op het edelmetaaloppervlak. Een kinetisch model, gebaseerd op elementaire stappen, is ontwikkeld.
dat in staat is de experimenten kwantitatief te beschrijven. Tevens is dit model gecombineerd met het gepubliceerde model voor de transiënte oxidatie van koolmonoxide over dezelfde katalysator, hetgeen de voorspelling van de gelijktijdige etheen en koolmonoxideoxidatie mogelijk maakt. Beide componenten reageren in tamelijk afzonderlijke zones, waarbij etheen alleen geoxideerd wordt als bijna alle koolmonoxide is omgezet. De deactivering van de katalysator door koolafzetting op het edelmetaal uit zowel etheen als acetylene is zowel kwalitatief als kwantitatief aangetoond door middel van LEIS experimenten. Het Pt oppervlak kon weer volledig worden gezuiverd door een behandeling met atomair zuurstof.

De kinetiek van de acetyleneoxidatie is onderzocht, zowel tijdens de stationaire toestand als onder transiënte condities over de Pt/Rh/CeO$_2$/γ-Al$_2$O$_3$ katalysator. Acetylene is gekozen vanwege de relatief hoge concentraties in een uitlaatgas tijdens de koude-start en vanwege de vertragende werking van acetylene op de ontsteking van de katalysator. Er zijn experimenten uitgevoerd in de gepakt bed reactor om de reactiesnelheidsparameters te bepalen. De experimentele condities gelijken op de koude-start van een benzinemotor. De experimenten in de stationaire toestand laten zien, dat acetylene zowel zijn eigen omzetting als die van zuurstof hindert. Koolmonoxide is het primaire reactieproduct van de acetyleneoxidatie. Tijdens de transiënte experimenten zijn voedingsstromen met acetylene en zuurstof gealterneerd over de reactor met frequenties tot 1/6 Hz. Twee typen geadsorbeerde acetylene lijken te bestaan. Net als bij de oxidatie van etheen is er ook bij de oxidatie van acetylene een selectieve degradatie van de katalysator voor zuurstofadsorptie gevonden, die te wijten is aan koolafzetting uit acetylene. Ceria bleek een belangrijke invloed te hebben op de oxidatie van acetylene. Kinetische modellen, gebaseerd op elementaire stappen, zijn ontwikkeld voor de omzetting van acetylene naar koolmonoxide, zowel tijdens de stationaire toestand als tijdens transiënte omstandigheden. Het transiënte model bestaat uit dezelfde stappen als het stationaire toestand model, met daaraan toegevoegd enkele stappen, die nodig zijn om verschijnselen te kunnen beschrijven, die niet onder de stationaire toestand kunnen worden geobserveerd. De beide modellen werden gecombineerd met de gepubliceerde kinetiek van de koolmonoxide oxidatie over dezelfde katalysator om de totale oxidatie van acetylene kwantitatief te kunnen beschrijven. Het stationaire toestand model geeft een redelijke beschrijving van de experimentele resultaten. Het gecombineerde transiënte model geeft ook een goede beschrijving van de simultane oxidatie van acetylene en koolmonoxide. Tijdens een transiënt reageren acetylene en koolmonoxide beide voornamelijk in een front, welke zich door de reactor begeeft, waarbij de aanwezigheid van koolmonoxide de omzetting van acetylene amper beïnvloedt.

De reductie van stikstofoxiden door koolmonoxide is onderzocht in aanwezigheid en afwezigheid van zuurstof door middel van transiënte experimenten bij koude-start condities over de commerciële Pt/Rh/CeO$_2$/γ-Al$_2$O$_3$ katalysator en daarvan afgeleide modellkatalysatoren. De hoge resolutie massaspectrometer werd gebruikt om onderscheid te kunnen maken tussen koolmonoxide en stikstof en tussen kooldioxide en lachgas. Mechanismen voor de verschillende katalysatoren zijn vergeleken. Een kinetisch reactieschema is voorgesteld, waarbij de verschillende bijdragen van de katalysatorbestanddelen naar voren worden gebracht. De kinetische snelheidsparameters zijn bepaald door middel van regressieanalyse van de transiënte experimenten. Het kinetisch model laat zien hoeveel zuurstof en stikstofoxide er door het ceria wordt opgenomen en afgestaan tijdens de rijke en arme deelperioden.

Het complete kinetische model voor de commercieel verkrijgbare autouitlaatgas-katalysator is ontwikkeld door de elementaire stappen modellen, zoals hierboven vermeld, samen te
voegen. Op deze manier bevat het model de oxidatie van koolmonoxide, etheen en acetylen en de omzetting van stikstofoxide naar stikstofdioxide, lachgas en stikstof. Het model is goed in staat om oppervlaktebedekkingen en gasfase concentraties aan het einde van de reactor in de tijd te voorspellen voor transiënte experimenten, waarbij één voeding de rijke componenten en de andere voeding de arme componenten bevat. Het model laat expliciet de invloed van ceria zien, in de vorm van opslag van zuurstof en stikstofoxiden en van bi-functionele reactie paden die de oxidatie van koolmonoxide, acetylen en etheen, en de ceria geassisteerde dissociatie van stikstofoxide beschrijven. Het effect van hoge concentraties water en kooldioxide is kwalitatief onderzocht. Kooldioxide verlaagt de activiteit van de katalysator, waarschijnlijk door reversibele adsorptie op het ceriaoppervlak. Water kan ook op ceria adsorberen, waar het de adsorptie van stikstofoxiden deels verhindert en de bi-functionele oxidatiepaden sterk versnelt. De oxidatie van koolmonoxide wordt het meest beïnvloed.

De verificatie van het model is uitgevoerd aan de hand van experimenten, gedaan bij condities die dichter bij echte autoutlaatgascondities liggen. Dit zijn experimenten met synthetische gasmengsels met reactorvoedingen rond \( \lambda =1 \) bij een frequentie van 1 Hz en bij zogenaamde arm-mengsel condities. De activiteit van de katalysator onder condities, waarbij ten alle tijde zuurstof aanwezig is, is lager dan het model voorspelt. Dit kan zijn omdat het edelmetaal in de katalysator reversibel geoxideerd wordt of door segregatie van Pt en Rh naar het katalysatoroppervlak. Aangezien deze chemische processen niet in het model verwerkt zijn, kan het model dit niet goed voorspellen.

Motorstandexperimenten (stoichiometrische- en arme ontsteking alsmede een \( \lambda \)-domeintest) zijn uitgevoerd om te onderzoeken of het model in staat is om het gedrag van de katalysator bij blootstelling aan echte autoutlaatgassen te voorspellen. De voorspellingen voor de stoichiometrische ontstekings- en de \( \lambda \)-domeintest zijn redelijk, maar de voorspellingen voor de arme ontsteking en de \( \lambda \)-domeintest zijn dat niet. De meeste voorspelde conversies zijn te laag, hetgeen aangeeft dat reacties, die niet in het model zijn opgenomen, zoals het versnellend effect van water, "steam-reforming" en "water-gas-shift" belangrijk kunnen zijn na de ontsteking van de katalysator.

Het gepresenteerde model is voldoende in staat de transiënte synthetische gas experimenten te voorspellen, waarbij één voeding een rijk mengsel en de andere voeding een arm mengsel bevat. Voor de correcte voorspelling van conversies van echte uitlaatgassen en synthetische mengsels, waarbij te allen tijde zuurstof aanwezig is, moet het model worden uitgebreid.
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NOMENCLATURE

\( A_i \)  
pre-exponential factor \( (/s^3) \) of rate coefficient \( k_i \)

\( A_i^b \)  
pre-exponential factor \( (/s^3) \) of backward step of reaction \( i \)

\( A_i^f \)  
pre-exponential factor \( (/s^3) \) of forward step of reaction \( i \)

\( a_{\text{cat}} \)  
washcoat surface area / \( m_{\text{NM}}^2 m_{\text{R}}^3 \)

\( a_r \)  
geometric surface area / \( m_{\text{R}}^2 m_{\text{R}}^{-3} \)

\( b \)  
parameter vector

\( b \)  
dilution ratio / \( m_{\text{inert}}^3 m_{\text{inert+cat}}^{-1} \)

\( C_i \)  
gas phase concentration of component \( i \) / \( \text{mol m}^{-3} \)

\( C_i^0, C_i(0) \)  
gas phase concentration of component \( i \) at reactor inlet / \( \text{mol m}^{-3} \)

\( c_p \)  
specific heat / \( J \text{kg}^{-1} \text{K}^{-1} \)

\( D_r \)  
reactor diameter / \( m_{\text{R}} \)

\( d_b \)  
monolith channel diameter / \( m_{\text{R}} \)

\( d_p \)  
pellet diameter / \( m_{\text{R}} \)

\( d_w \)  
washcoat thickness / \( m_{\text{R}} \)

\( e \)  
charge of one electron /-

\( E_a, E_{a,i} \)  
activation energy \( (/J \text{mol}^{-1}) \), of rate coefficient \( k_i \)

\( E_i^b \)  
activation energy \( (/J \text{mol}^{-1}) \) of backward step of reaction \( i \)

\( E_i^f \)  
activation energy \( (/J \text{mol}^{-1}) \) of forward step of reaction \( i \)

\( F_i \)  
F-value for model \( i \) (statistical) /-

\( F_i^0 \)  
inlet molar flow rate of component \( i \) / \( \text{mol s}^{-1} \)

\( F_{\text{TOT}} \)  
total molar flow rate / \( \text{mol s}^{-1} \)

\( f \)  
frequency of oscillation /Hz

\( g \)  
model calculation

\( g_q \)  
model calculation of response \( q \)

\( i.d. \)  
internal diameter / \( \text{mm} \)

\( K_i \)  
equilibrium coefficient for reaction step \( i \), \( k_i^f/k_i^b / \text{m}^3/\text{mol} \)

\( k_f \)  
mass transfer coefficient / \( m_{\text{R}}^3 m_{\text{R}}^{-2} \text{s}^{-1} \)

\( k_i \)  
rate coefficient for reaction step \( i \)

\( k_i^f, k_i^b \)  
forward, respectively backward, rate coefficient of reaction step \( i \)

\( l \)  
length / \( \text{mm} \)

\( L_k \)  
capacity of catalyst phase \( k \) / \( \text{mol} \text{kg}^{-1} \text{CAT} \)

\( L_r \)  
reactor length / \( m_{\text{R}} \)
Nomenclature

\( M \)  
number of reaction steps /-

\( M_i \)  
molar mass of component \( i \) /kg mol\(^{-1}\)

\( n \)  
number of masses measured simultaneously with the Quadrupole Mass Spectrometer /-

\( p_i \)  
partial pressure of component \( i \) /kPa

\( p_i^0 \)  
reactor inlet partial pressure of component \( i \) /kPa

\( p_i^1 \)  
reactor outlet partial pressure of component \( i \) /kPa

\( p_{\text{TOT}} \)  
total pressure /kPa

\( P \)  
pressure /Pa

\( R \)  
gas constant /J mol\(^{-1}\) K\(^{-1}\)

\( R_i \)  
production rate of component \( i \) /mol mol\(^{-1}\) \( \text{NM,surf} \) s\(^{-1}\)

\( R_{k,i} \)  
production rate of component \( i \) corresponding to catalyst phase \( k \) /mol mol\(^{-1}\) s\(^{-1}\)

\( R_{\text{w},i} \)  
specific production rate of component \( i \) /mol kg\(^{-1}\) CAT s\(^{-1}\)

\( r_{k,j} \)  
reaction rate of reaction step \( j \) corresponding to catalyst phase \( k \) /mol mol\(^{-1}\) s\(^{-1}\)

\( r_{\text{w},j} \)  
specific reaction rate of reaction step \( j \) /mol kg\(^{-1}\) CAT s\(^{-1}\)

\( S \)  
objective function

\( S_{\text{CO}} \)  
selectivity towards carbon monoxide /-

\( s_0 \), \( s_{0,i} \)  
sticking probability, of component \( i \) /-

\( T \)  
temperature /K

\( t \)  
time /s

\( W \)  
catalyst mass /kg\(_{\text{CAT}}\)

\( w_{i,q} \)  
weight factor of response \( q \) for experimental observation \( i \) /-

\( x \)  
distance from the top of the catalyst bed in the direction of the reactor axis /mm

\( x_i \)  
vector of set variables for experiment \( i \)

\( X_i \)  
conversion of component \( i \), \((p_i^0 - p_i^1)/p_i^0 /-

\( y_i \)  
\( i^{\text{th}} \) experimental observation

\( y_{i,q} \)  
\( i^{\text{th}} \) experimental observation of response \( q \)

\( y_{i}(k) \)  
dependent variable \( i \) at grid point \( k \)

\( z \)  
dimensionless reactor length /-, defined as the cumulative catalyst mass divided by the total catalyst mass

\((\Delta H)\)  
reaction enthalpy / J mol\(^{-1}\)

Greek symbols

\( \alpha \)  
heat transfer coefficient / W m\(^{-2}\) K\(^{-1}\)

\( \beta \)  
factor indicating the activation energy dependence on surface composition / J mol\(^{-1}\)

\( \delta_n \)  
degree of surface coverage of component \( n \) adsorbed on the support capacity /-, defined as the amount of adsorbed species \( i \) divided by a monolayer capacity

\( \delta_e \)  
degree of empty support sites /-

\( \epsilon \)  
monolith converter void fraction / m\(^3\) m\(^{-3}\)

\( \epsilon_B \)  
bed porosity /m\(^3\)_gas m\(^3\)_R

\( \epsilon_w \)  
washcoat porosity / m\(^3\)_w m\(^3\)

\( \zeta_i \)  
fractional coverage of the species in the ceria sub-surface layer

\( \zeta_m \)  
fraction of vacant sites in the ceria sub-surface layer
Nomenclature

\[ \theta_C \] fraction of the total exposed noble metal covered with carbonaceous deposits

\[ \theta_i \] degree of surface coverage of component \( i \) adsorbed on the noble metal capacity, defined as the amount of adsorbed species \( i \) divided by a monolayer capacity

\[ \theta_i^C \] fractional surface coverage of component \( i \) on the noble metal covered by carbonaceous deposits

\[ \theta_e \] degree of empty noble metal sites

\[ \lambda \] relative air/fuel ratio compared to stoichiometry

\[ \lambda_s \] solid phase heat conduction coefficient \( /J \, m^{-1} \, s^{-1} \, K^{-1} \)

\[ \nu_{ij} \] stoichiometric coefficient of surface species \( i \) in reaction step \( j \)

\[ \xi_i \] degree of surface coverage of component \( j \) adsorbed on oxygen storage capacity (ceria), defined as the amount of adsorbed species \( i \) divided by a monolayer capacity

\[ \xi_s \] degree of empty oxygen storage sites

\[ \rho \] density \( /kg \, m^{-3} \)

\[ \rho_B \] bed density \( /kg_{CAT} \, m^{-3} \)

\[ \sigma \] stoichiometric number

\[ \tau \] residence time, \( \epsilon_B \, W_{CAT} / (\rho_B \, F_{TOT} \, V_{mol}) /s \)

\[ \Phi_{m}^{\sup} \] superficial mass flow \( /kg \, m_R^{-2} \, s^{-1} \)

Subscripts

a adsorption

ads adsorption

B bed

C on carbonaceous deposits

CAT catalyst

CeS ceria surface

CeB ceria sub-surface

d desorption

ER Eley- Rideal

f bulk gas phase

k catalyst phase \( k \)

LH Langmuir-Hinshelwood

NM noble metal

OSC oxygen storage capacity

outlet reactor outlet

r reactor

s surface

SUP support

TOT total

w washcoat

Superscripts

0 reactor inlet

1 reactor outlet
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>b</td>
<td>backward</td>
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<tr>
<td>f</td>
<td>forward</td>
</tr>
<tr>
<td>tot</td>
<td>total</td>
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Abstract
The slow catalytic reaction kinetics during the cold-start period of an automotive exhaust gas converter lead to emission of harmful gases into the environment. In order to optimise the operation of the current converter, detailed kinetic knowledge is required. The dynamic nature of the converter operation requires the use of transient kinetic procedures to develop accurate kinetic models. Such models can be used to create a model predictive controller. Elementary step models are generally more accurate than empirical models and give more insight into the catalytic processes. Current literature in this respect mainly focuses on single reactions and on steady state conditions. Models using complex exhaust gases are mostly based on empirical kinetics. This thesis presents a transient elementary step model, obtained over one commercial catalyst for an exhaust gas, consisting of hydrocarbons, carbon monoxide, and nitric oxides.

1.1. Automotive exhaust gas issues
The continuous expansion of road traffic causes an on-going demand for less pollution from automotive engines, reflected by increasingly severe legislation (Shelef & McCabe, 2000; Greening, 2000; Bertelsen, 2000). The pollutants are toxic and contribute to the formation of smog and acid rain, and may also lead to an increase of the greenhouse effect. The removal of these harmful components from Otto engine exhausts is commonly achieved by the application of a so-called three-way catalytic converter. These catalysts allow a simultaneous conversion of hydrocarbons, carbon monoxide, and nitrogen oxides into carbon dioxide, water, and nitrogen, and are very effective at stoichiometric feed conditions once the catalyst has reached a sufficiently high temperature (Taylor, 1993; Tamaru & Mills, 1994). Under cold start conditions, i.e. before the light-off of the monolith, the currently employed converters cannot eliminate all pollutants. The low temperature of the catalytic surface causes too slow reaction kinetics to achieve full conversion of all pollutants (Zygourakis, 1989). The conversion of all pollutants is determined completely by the chemical kinetics under these conditions.
A detailed understanding of the relevant reaction mechanisms and kinetic processes, taking place simultaneously and interactively at cold-start conditions, could assist in the optimisation of the catalyst converter and/or the catalytic formulation, as well as the development of new control strategies (Balenovic et al., 1999). Using the kinetic model, an optimal motor management system can be developed, in order to reduce emissions still further. Optimal emission reduction may be achieved when the Oxygen Storage Capacity (OSC) of the catalyst is only partly filled under all circumstances. The filled fraction can, however, not be measured directly. A controller, which contains a dynamic model for the catalyst, is able to calculate the degree of OSC filling, using available sensor data only. On the basis of the model, the engine can be controlled extremely tightly in order to obtain the desired behaviour. As model errors will be immediately transferred into controller errors, very accurate and stable kinetic models are necessary.

Such models require knowledge of the intrinsic transient kinetics on the basis of elementary reaction steps, as a result of the dynamic character of the converter operation. During catalyst warm-up especially, the operating conditions change continuously, resulting in alterations of the rate-determining step (Silveston, 1995). Moreover, oscillations of the reactor feed composition with frequencies of about 1 Hz (Taylor & Sinkevitch, 1983), as induced by the lambda controller, cause transient effects that influence the time-averaged conversion due to the non-linear character of the kinetics. Finally, the behaviour of the driver introduces transient phenomena, and these are usually accounted for by typical dynamic tests like FTP and European driving cycles. These transients affect the converter performance via the space velocity and the exhaust gas temperature.

The number of reported transient kinetic studies is still not very large (e.g. Sant & Wolf, 1989; Sadhankar & Lynch, 1996; Maunula et al., 1997). The calculations necessary to obtain the rate parameters for transient kinetic models are very complicated and time demanding (Nowak et al., 1996; Kirchner & Eigenberger, 1997). Transient models based on elementary reaction steps for plug flow reactors contain a differential equation for each gas phase compound and each surface species at all grid-points in the reactor. The steep transients require the time-grid to be extremely small, leading to thousands of differential equations to be solved every experimental second. This is reason for many authors to use simplified or empirical model equations (e.g. Hinz et al., 2000; Dubien & Schweich, 1998; Granger et al., 1998). This limits the use of those models to the range of experimental conditions in which they were determined. Also, many authors choose not to present a quantitative model, but to only present a chemical model, consisting of a number of chemical reaction steps. These type of publications often provide very useful information to base kinetic models on (e.g. Oh et al., 1986, Oh 1990; Maunula et al., 1997; Cho, 1994).

1.2. Elementary step modelling

These transients, mentioned in the previous section, lead to the demand that one and the same exhaust gas reactor should operate properly under a wide variety of conditions. This is a remarkable difference with other chemical reactors, that usually operate in a steady state at predefined conditions within a rather narrow window (Lox et al., 1991).

Many studies on automotive converter modelling use steady state kinetic rate equations. In particular the classical work of Voltz et al. (1973) is often applied, which should be considered as empirical, since not based upon a mechanism (Schweich, 1995; Dubien &
Introduction

Schweich, 1998). The transient aspect of automotive converter operation is important for reactor simulation and design as far as the choice of kinetic models is concerned. The assumption, whether steady state reaction kinetics can be used in the transient state, is questionable for reasons of oxygen storage in ceria, oxidation and reduction of rhodium, reversible poisoning, and transient surface phenomena in general (Siemund et al., 1996). Transient operation involves accumulation terms in a reactor model, both for gas phase components and for surface species. This requires reaction kinetics based upon elementary steps, because the classical steps of a catalytic reaction, e.g. adsorption, surface reaction, desorption, do not proceed at the same rate. Approximations via Langmuir-Hinshelwood or Eley-Rideal type of rate equations could be applied in case of one rate determining step (e.g. Nibbelke et al., 1997a,b; Burch & Watling, 1997; Chapter 4). Such an approach, however, may fail even in a steady state, since different steps may become rate controlling if concentrations change considerably from reactor inlet to outlet, as to be expected for zero-emission vehicles. CO oxidation over noble metals is a well-known example of a reaction with an order +1 in CO at low CO concentration, but –1 for high concentrations (Nibbelke et al., 1997a). Different rate determining steps may also arise if operating temperatures change considerably (Schweich, 1996), because adsorption usually is not an activated process, while surface reaction and desorption rates often obey Arrhenius behaviour. Such behaviour may occur along the reactor axis, because temperature differences of 150 K between reactor inlet and outlet are not exceptional. After a cold engine start, reactor temperatures may rise from below room temperature up to 700 K and more.

Therefore, the experimental conditions used to extract the kinetic data are very important. Next to temperatures (e.g. Comrie & Lambert, 1974 and Sadhankar & Lynch, 1997) also the choice of model hydrocarbons (Bart et al., 1992; Obuchi et al., 1996), addition of water (Nibbelke et al., 1997; Marécot et al., 1994), and the presence of carbon dioxide and sulphur dioxide (Bart et al., 1992; Mabilon et al., 1995) play an important role. Many publications describe only one particular reaction, e.g. carbon monoxide oxidation (e.g. Nibbelke et al., 1997a; Berlowitz et al., 1988; Bonzel & Ku, 1973; Bunluesin et al., 1996). By this means, it is only possible to construct a complete model from several sub-models, when all these sub-models are based on elementary reaction steps (Nievergeld et al., 1997).

The foregoing pleads for kinetic modelling on the basis of elementary steps because of the larger impact of such models. An even more important advantage of elementary step modelling is that a model can be determined experimentally for one global reaction, but applied in a combination of elementary step kinetics for other global reactions. In this way mutual interactions between different global reactions, as may happen because of common gas phase components or surface species, can be simply accounted for. An automotive exhaust gas is an example of such a complicated reacting mixture, where many competing reactions occur simultaneously. Oxygen adatoms may arise from gaseous oxygen or nitric oxide, and may be consumed by hydrogen, carbon monoxide, or many hydrocarbons with different affinities for oxygen. Elementary step kinetics may incorporate the effects of distinct hydrocarbons, as they include steps for the reduction of NO by hydrocarbons.

The wide variety of catalysts with different noble metals (e.g. Pt, Rh, Pd or alloys), different carriers (e.g. CeO₂, ZrO₂ and Al₂O₃), and even different pre-treatment procedures may lead to very different results (e.g. Granger et al., 1998; Oh, 1990; Bunluesin et al., 1996; van Slooten & Nieuwenhuys, 1990, and Chapter 5). Reaction mechanisms may generally be similar over different noble metal catalysts, but kinetics strongly depend on the type of noble metal. For
alloys, even the noble metal composition is important (e.g., Bart et al., 1992, and Amon-Meziere et al., 1995).

Modelling via elementary steps also allows to adapt the kinetic model when the catalyst formulation is changed in order to introduce new catalytic functions. A typical example is the introduction of ceria into the three-way catalyst, which takes care of the so-called bifunctional reaction path between carbon monoxide on the noble metal surface and oxygen adatoms from the ceria lattice. This path has been proven important at high CO and low O\textsubscript{2} concentrations (Nibbelke et al., 1997; Zafiris & Gorte, 1992).

Kinetic modelling on the basis of elementary steps exploits the law of mass action, which is the best possible rate equation. It is sometimes argued that elementary step kinetics contain so many parameters that any description of experimental data becomes within reach. It should be realised, however, that each step preferably is proven relevant on the basis of experimental evidence, and quite often such relevance has already been reported in the literature from studies that applied completely different techniques. Moreover, the rate parameters should have significant values from a statistical point of view, as to be obtained from multi-response non-linear regression, and these values should be consistent with well-established theories. Elementary step kinetics have already been proven very effective in modelling gas phase chain reactions, whether or not catalytically initiated, like hydrogen (Warnatz & Gardiner, 1984) or methane (de Smet et al., 2000) oxidation, or oxidative coupling of methane (Couwenberg et al., 1996).

Steady state kinetic studies may provide limited information on the rate coefficients of the underlying mechanistic steps, as those coefficients can get lumped if some step should be considered as rate determining or instantaneous. During kinetic measurements under transient conditions, reactor outlet responses to perturbations at the reactor inlet are observed in real time. In principle, such experiments contain more information on individual reaction steps (Bennet, 2000), as all steps may proceed at different rates after imposing the perturbation, and each step may temporarily become dominant during the relaxation process.

Transient kinetic methods apply pulse type of perturbations, as in Temporal Analysis of Products (TAP) (Gleaves et al., 1988), or stepwise perturbations, which is well-known as cycling of the feed (Silveston, 1998). A special stepwise perturbation concerns Steady State Isotopic Transient Kinetic Analysis (SSITKA) (Happel, 1986; van Dijk et al., 2000). A reactant in the feed is replaced by an isotopic variant, which allows the reactor to be operated in a chemical steady state, while the interaction of the reactant with the catalyst can be monitored via mass-spectrometry at the reactor outlet.

A major drawback of transient kinetic studies concerns time and costs involved, due to the more complicated character of the experimental set-up, the experiments themselves and their interpretation. In fact, these studies should be performed only for the major fast processes involved in exhaust gas conversion, while slow processes can be added to converter models via a quasi-steady state approach. Because of the large number of parameters involved, full transient models might be simplified on the true basis of a sensitivity analysis, for verification with other catalysts. Such model simplifications could be implemented in more sophisticated control strategies. As on-board computational capabilities continue to increase, self-diagnostic features will be incorporated in the control system to compensate for catalyst ageing and sensor response characteristics (Shelef & McCabe, 2000).
1.3. Scope of this thesis

This thesis focuses on dynamic modelling of automotive exhaust gas reactions over a single catalyst Pt/Rh/CeO₂/γ-Al₂O₃. The work intends to settle a kinetic model on the basis of elementary steps with quantification of rate parameters. It is capable of predicting reactor outlet concentrations in time, given a certain time dependent reactor feed. The model also provides predictions of the surface coverages of the noble metal and ceria.

The model could be applied in the design/optimisation of catalytic converters or for development of a new converter control strategy as mentioned before. It can be extended by adding new steps, accounting for new catalytic functions of improved formulations, or new effects that are considered as relevant for similar catalysts. Also, it could be simplified for a well-defined small range of conditions by elimination of steps, less relevant during these conditions. Furthermore, the model could be adapted for use in different catalyst formulations, e.g. different amount or ratio of noble metals or different support, if the mechanisms are assumed not to be altered largely. The latter could be realised by re-optimisation of the rate parameters on the basis of a relatively small number of transient experiments over the new catalyst formulation.

The kinetic model consists of four separate sub-models:
1) the oxidation of carbon monoxide, which has been described in detail by Nibbelke et al. (1998),
2) the oxidation of ethylene, which is described in Chapter 3,
3) the oxidation of acetylene, which is described in Chapter 4,
4) the reduction of nitric oxide, which is described in Chapter 5.

These four sub-models have been combined to form a complete model for an automotive three-way catalyst (Chapter 6), which was tested for conditions, that approach practical automotive exhaust gas conditions. The word "complete" in the previous sentence has been italicised, because its completeness can be argued:

- No hydrogen oxidation has been inserted into the model, while it is known that automotive exhaust gases contain up to 0.23 vol. % hydrogen (Taylor, 1993). Often, the influence of hydrogen is assumed to be only a heat effect, which is then corrected for by assuming a larger oxidation heat for the CO oxidation (Kuo, 1971; Zygourakis & Aris, 1983). This assumption however is disputable (van Gemert et al., 1997). Another reason, not to include hydrogen into the model, is the experimental difficulty to measure both hydrogen and water quantitatively with a mass spectrometer.

- A real exhaust gas contains hundreds of different hydrocarbons (Kubo et al., 1993; Drake et al., 1996), while the model described in this thesis contains only two. It is obvious that a choice had to be made. Ethylene has been chosen to represent the hydrocarbons, which can be oxidised quite easily. According to Impens (1987), a cold start automotive exhaust gas contains approximately 25 mol % ethylene. Furthermore, it was found (Mabilon et al., 1995; Bart et al., 1992) that aromatics, which represent another 20 mol % of hydrocarbons in an exhaust gas, display similar oxidation behaviour as ethylene. Acetylene (also 20 mol %) was chosen mainly because of its large inhibitive effect after a cold engine start. Acetylene has to be included if one focuses on the light-off behaviour. If aromatics indeed display similar oxidation behaviour as ethylene, it could be said that the model covers 65% of all hydrocarbons. Methane, which contributes another 20 mol %
can be regarded as inert at cold start conditions (de Smet et al., 2000; Bart et al., 1992; Oh et al., 1992). This leaves 15 mol % of the hydrocarbons uncovered, including other alkanes, which will hardly adsorb onto the catalyst surface during cold-start conditions (Burch & Watling, 1997; Bart et al., 1992). Summarising, it could be said that ethylene and acetylene are excellent representatives for hydrocarbons in an exhaust gas, reacting at cold-start conditions.

- Another lack of the model is the absence of describing the effects of large amounts of water and carbon dioxide. A real automotive exhaust gas contains approximately 13 vol. % water and 14 vol. % carbon dioxide (Taylor, 1993). The influence of water and carbon dioxide is not straightforward. According to Lemaire et al. (1995), water and carbon dioxide do not influence the reduction of NO by CO over Pd. For the oxidation of hydrocarbons it is sometimes assumed (Marécot et al., 1994) that water simply decreases the total available number of active sites on the catalyst. Water-gas-shift and steam-reforming reactions only occur at temperatures above 573 K (Nibbelke et al., 1997a,b). In the steady state, the oxidation of carbon monoxide was accelerated and the oxidation of ethylene was decelerated by the presence of water (Nibbelke et al. 1997a,b). Isotopic labelling experiments, using $^{18}$O$_2$ yielded mainly H$_2^{18}$O instead of the expected C$^{18}$O$^{16}$O (Campman, 1996). The presence of carbon dioxide mainly decreases the oxidation rate of all reactions (Nibbelke et al., 1997a,b), which may be contributed to carbonate formation on ceria, although this cannot explain the decreased reaction rate of ethylene oxidation at low temperature, which does not involve a bifunctional path (Nibbelke et al., 1997b, Chapter 3).

These examples indicate that both water and carbon dioxide are involved in complex mechanisms, which contribute, either positively or negatively, to the reactions taking place at the catalytic surface. Chapter 6 of this thesis gives an introduction into this complex field, on the basis of a number of experiments. The quantification of the effects of water and carbon dioxide, on the basis of elementary reaction steps, is an advisable topic for future research.

- Exhaust gases also contain between 5-30 ppm SO$_2$ (van Selow, 1996). According to Bart et al. (1992) and Mabilon et al. (1995), SO$_2$ will adsorb onto the catalyst, where it poisons the oxidation of hydrocarbons. According to Whittington et al. (1995) also steam reforming and water gas shift reactions are poisoned by the presence of sulphur. Boaro et al., (2000) investigated the influence of SO$_2$ on ceria containing catalysts, where also the oxygen storage capacity decreases. They found that SO$_2$ will poison the catalyst, especially at low temperatures; the sulphur can only be removed at temperatures above 673 K. This indicates that for cold-start conditions, sulphur has quite a large influence on the conversion of all reactants. The reason it has not been introduced into the model, presented in this thesis, is because of the difficulties in acquiring reproducible data with sulphur containing exhaust gases. Also, possible poisoning of the analysis equipment has been an important reason to omit SO$_2$. For more realistic model calculations during cold-start conditions, it is probably justified to model the influence of SO$_2$ by decreasing the noble metal surface capacity as well as the ceria surface capacity.

1.4. Challenges: balancing between surface science and real engines exhausts

The demand for a detailed kinetic model, which can be successfully used for the prediction of pollutant conversion over a commercial automotive exhaust catalyst in an extremely wide
range of conditions, causes a number of challenges. The most thorough and detailed way
would be to study the kinetics via a surface science approach. The related measurement
techniques, however, do not allow experiments at pressures and pollutant concentrations as
met under real exhaust gas conditions: mostly single crystals of Rh or Pt are investigated
under Ultra High Vacuum conditions, using various spectroscopic analysis techniques, like
SIMS and TPD (e.g., Hopstaken & Niemantsverdriet, 2000). The results contain extremely
detailed information on the surface compositions and kinetic behaviour of the components at
the investigated conditions. This is both the strength and weakness of the approach. Largely
empty surfaces, vacuum conditions, and single crystal catalysts provide an ideal system for
experiments, but are serious deviations from the conditions found under real automotive
conditions.

Another approach would be to study the behaviour of real exhaust gases from an Otto engine
set-up. This approach would allow measurements under the most realistic conditions
possible. However, also this approach has disadvantages: the composition of the engine
exhaust gas will vary with the applied conditions and the catalyst will quickly deteriorate
because of high temperatures and compounds like sulphur in the gasoline. This poses
difficulties to obtain reproducible measurements. Also, the large variety of components in the
exhaust gas will make modelling extremely complex, since observed phenomena are
obscured by mutual interactions. The results will consist of a (semi-) empirical model, only
usable for a limited range of conditions. No information about kinetic and mechanistic
aspects of the catalytic mechanism can be derived from such models (e.g., Jirát et al., 1999).

The approach as used in this study, viz., transient kinetic experiments in a catalytic fixed bed
reactor, could be seen as a compromise between the two approaches. It combines the
advantages of both, but unfortunately also some of the disadvantages. The conditions like
temperatures, gas phase concentrations, pressures and transients resemble real automotive
exhaust gases, but the "exhaust" gases are synthesised through mass flow controllers and,
hence, are simplified, which is a step away from reality. Components, however, which make
interpretation more difficult, like water, can be eliminated in one experiment and added in
another one. Modelling can be performed on the basis of elementary steps, but requires a
rather complex chemical model, in order to adequately describe most important phenomena
from the experiments. Contrary to empirical and steady state models, this generates a large
number of kinetic parameters, each of them being responsible for describing a part of the
transient. Model calculations become very complicated since every gas phase component, as
well as every surface species requires a differential equation. This set of highly stiff non-
linear differential equations must be solved simultaneously in time and space, which demands
a large amount of computing time, in particular when the model solution is coupled to non-
linear regression of the data in order to extract quantitatively the rate parameters. Such
regression may fail, if it ends in one of the many local minima of the sum of square space.
Techniques like random search or genetic algorithms may overcome this problem, but require
even more computing time.

Using fewer parameters, i.e. a more simple model, causes a less adequate prediction of at
least a part of the experimental data. The regression technique to determine the parameters
does not allow the use of more parameters then is supported by the experiment. This leads to
a number of approximations, which sometimes results into steps in the model, which are not
elementary. This can be summarised with the statement that exactly the number of parameters
is used required to obtain an adequate description of the experimental data, not more nor less.
An important issue in kinetic studies is the applied temperature range. Too low temperatures cause near zero conversion, while high temperatures result in high conversion leading to a non isothermal catalyst bed and/or non intrinsic kinetics. The relevant temperatures for experiments depend on the mixture fed to the reactor. Nibbelke et al. (1998) used temperatures between 393 and 433 K for transient CO oxidation, and also ethylene oxidation (Chapter 3) was studied in the same temperature range. For acetylene oxidation (Chapter 4), however, temperatures between 503 and 543 K had to be used in order to obtain significant conversions. NO conversion (Chapter 5) required temperatures from 523 to 573 K. For a combination of all sub models, the rate parameters for CO and ethylene oxidation must be extrapolated over more than 100 K, which appeared inaccurate for some steps. This issue was solved by correcting the corresponding rate parameters, by creating a kind of compromise that predicts reasonable rate coefficients at both low and high temperature. This makes the model usable for a large temperature range, as is necessary for modelling the cold-start period.

Other assumptions made in the modelling are the absence of lateral interactions and of island formation, the restriction to one monolayer adsorption, and negligence of mechanistic and kinetic differences between Pt and Rh sites. For CO (Oh et al., 1986; Berlowitz et al., 1988) and hydrocarbon oxidation, reaction kinetics may be comparable, but this is certainly not the case for NO reduction (e.g. Chapter 5). The assumption that these sites are equal will lead to rate parameters which are not correct for Pt or for Rh, but only for the Pt/Rh ratio of the used catalyst.

The question can then be raised about the value of a model, which contains so many assumptions, obtained under non-real exhaust conditions. For practical purposes the model is indeed very valuable. For the applied catalyst it can be used without problems to predict pollutant conversions. Also, it can be simplified for smaller ranges of conditions. For other catalyst formulations the model can be re-optimised and additional steps can be added for additional functions of more elaborate catalysts, e.g. addition of Zr to the ceria or BaO for NO storage.

From a more fundamental point of view, the model is interesting as it shows the behaviour of reaction steps used in this model, most often found in surface science studies, under atmospheric pressures and in combination with other surface species. Also, it gives detailed insight into possible transient behaviour of such steps. This way it demonstrates the power of the elementary step modelling.

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EXPERIMENTAL SET-UP AND EQUIPMENT

The application of the magnetic sector mass spectrometer has been submitted to Review of Scientific Instruments.

Abstract
The experimental set-up used to perform the transient kinetic experiments is described. This set-up contains two separate gas inlets, which enable fast switching between rich and lean reactor feeds. Special attention is paid to the analysis system, where a high-resolution magnetic sector mass spectrometer has been used. This instrument allows separation of the isobaric masses of CO and N₂ as well as CO₂ and N₂O, which are separately monitored in time. This enables to determine individual rate parameters for reactions of all gaseous components. A description of the hardware set-up as well as the used software is given.

2.1. Introduction

In order to obtain transient kinetic models, a dedicated experimental set-up and on-line analysis equipment are required. The transient data have been obtained by performing feed cycling experiments, generally by alternating a rich feed (= oxygen poor) with a lean feed (= oxygen rich) over a reactor, containing a catalytic fixed bed. The inlet system is equipped with two sets of mass flow controllers, one for each feed, in order to independently create two different gas compositions.

The reactor has been designed to approach plug flow behaviour. This is an important requirement, because mixing of gases would disturb the transient signals, as measured by the analysis equipment. The plug flow character is enhanced by using high gas flow rates (5.6 mmol/s) leading to a very short reactor residence time (8 ms). Also, the assumption of plug flow will facilitate the modelling, because convection is the only significant transport mechanism in an ideal plug flow reactor.

When switching between two reactor feeds, each having a different composition, the overlap between the feeds during the switch, should be minimal, in order to avoid mixing of the separate feed gases as much as possible. For this reason, fast magnetic valves, which open and close in approximately 4 ms, have been used for switching between the two reactor feeds.
The feed which is not fed to the reactor is directed to the ventilation of the set-up in order to avoid pressure changes after the feed switches. These pressure changes can disturb the transient signals. For the same reason, the flow resistance of both exhaust lines (through the reactor and directly to the vent) has been equalised. The total pressure in the reactor is always kept equal to 110 kPa, because the mass spectrometer analysis is sensitive for (partial) pressure changes. Also, the use of a constant pressure will facilitate the modelling. The catalyst bed is prepared in such a way that the pressure drop over the bed is less than 5% of the inlet pressure.

Figure 2.1. Schematic view of the experimental set-up. The left part shows the duplicate gas blending system, where each gas is fed through a mass flow controller. Water can be added by means of two HPLC pumps feeding water to the evaporators. By means of four electromagnetic valves, the two feeds with different composition are alternated over the catalyst bed (middle part), with an adjustable frequency up to 10 Hz. Two capillaries, in front of and behind the reactor, are connected to the on-line mass spectrometer via a three-way valve, allowing to monitor either the reactor inlet or the reactor outlet concentrations in real-time. The on-line gas chromatograph is used for steady-state measurements. The reactor is placed in an oven, and can be operated at a maximum temperature of 773 K.

The isothermnicity of the reactor is always verified during the experiments. Temperature profiles in the axial and/or radial direction of the reactor could have a profound influence on observations, and should therefore be avoided. In practice, a temperature difference between the reactor inlet and outlet and between the reactor centre and the reactor wall of 5 K is allowed.

To develop transient kinetic models, accurate concentration measurements of responses to concentration inlet perturbations are vital. They require analytical equipment that allows
quantitative measurements with high time resolution, because large and fast gas phase concentration changes occur in an automotive converter, due to the response time of the lambda probe, which causes oscillations around stoichiometry at a frequency of about 1 Hz (Herz, 1981). In order to be able to measure such fast changes accurately, a sampling frequency of about 50 Hz is required. This value is required in order to obtain sufficient data points (i.e. 5 data points at a switch from 0 to 0.5 vol. % in 0.1 s) on the slopes which occur when switching from one feed to another, as is the case for the experimental set-up used in this study. Additionally, according to Nievergeld (1998), reactions with a typical time constant of 40 ms may occur. Using a sampling frequency of 50 Hz would then yield two measurement points during this time. High stability, sensitivity, and signal/noise ratio are also necessary, because of the low concentration levels striven for in zero emission vehicles. Furthermore, the gas sampling system should not disturb the plug flow character of the total system.

The experimental set-up has been described in detail before by Campman (1996) and is schematically depicted in figure 2.1. It consists of feed, reactor, and analysis sections.

2.2. Inlet system

The feed section consists of two duplicate gas blending systems to generate two feed streams with different compositions. For each component, a blending system contains an electromagnetic valve and a thermal gas mass flow controller. Six different gases can be fed through both inlets. Two HPLC pumps in combination with water evaporators allow to add steam to both feed streams.

By means of four magnetic valves, the two gas feeds are alternated over the reactor with an adjustable frequency up to at least 10 Hz. The outlet system has been constructed in such a way that pressure changes during switching are minimal.

2.3. Reactor section

The reactor section consists of a tubular preheater and a stainless steel fixed bed reactor (type 316). A cross section of the reactor is depicted in figure 2.2. The two feed lines remain separated in the preheater up to the catalyst bed and are sealed off by sapphire beads, unless the beads are pressurised. This allows only one gas flow to be led over the reactor. The catalyst bed has a length of 15 mm and a diameter of 13 mm. Sample chambers, immediately above and below the catalyst bed are connected via capillaries to the on-line mass spectrometer for real-time analysis. A thermocouple tube allows monitoring the axial temperature profile in the catalyst bed, in order to assure isothermal experiments. Radial temperature profiles are monitored by a thermocouple located on the outside reactor wall. This latter thermocouple is used as input for a PID controller, which sets the reactor temperature by controlling two infrared radiators. The reactor pressure is manually controlled by a spring loaded back-pressure valve and measured downstream the reactor. The total pressure in the reactor is kept constant at 110 kPa, and He is used as bulk gas. The total gas flow rate through both feed lines always equals 5.6 mmol/s, resulting in a reactor residence time of about 8 ms.
Figure 2.2. Detailed cross section of the laboratory reactor. Two sets of sapphire beads (only two beads are shown) seal off the reactor inlets unless pressurised, thus enabling nearly perfect step changes. In the sample chambers, just above and below the catalyst bed, the capillaries connected to the mass spectrometer are mounted, allowing to monitor the reactor inlet and outlet concentrations.

2.4. Catalyst

The Pt/Rh/CeO$_2$/γ-Al$_2$O$_3$ three-way catalyst (as used for coating monoliths) and its derived model catalysts Pt/γ-Al$_2$O$_3$ and Pt/Rh/γ-Al$_2$O$_3$ were provided by dmcc A.G. (Germany) as a powder with a mean pellet diameter of 12 µm. The catalysts consist of 0.398 wt. % Pt, 0.080 wt. % Rh (if applicable) and 28 wt. % CeO$_2$ (if applicable).

The powder was pressed, crushed and sieved to obtain a fraction with pellet diameters between 0.11 and 0.15 mm. The reactor contained typically 0.9 g of catalyst and 1.4 g of inert α-Al$_2$O$_3$ (0.15 - 0.21 mm) for dilution. The catalyst was pre-treated at 773 K in oxygen for one hour followed by reduction with hydrogen for two hours. More details have been reported elsewhere (Campman, 1996).

Reproducible experimental data could then be obtained by keeping the catalyst continuously under transient conditions, alternating between a rich feed and a lean feed, hence avoiding the slow deactivating oxidation of the noble metal particles (Carbello & Wolf, 1978; Burch & Hayes, 1995; Hiam et al., 1968). All experiments were carried out under conditions for intrinsic chemical kinetics, when judged with well-known criteria that were developed for steady state kinetic research. For the majority of data, the intrinsicity will not be affected by cycling of the feed (Hoebink et al., 1999), although this cannot be guaranteed shortly after switching from one feed to the other.

2.5. Analysis section

The analysis section consists of an online gas chromatograph (Carlo Erba Instruments GC 8340) for steady state measurements and an online quadrupole mass spectrometer (VG Sensor lab 200D) for steady state and transient measurements. The mass spectrometer measured the He, C$_2$H$_2$, C$_2$H$_4$, CO, O$_2$, and CO$_2$ concentrations both at the reactor inlet and outlet during the cyclic feeding experiments (chapters 3 and 4). Analysis can be done with a frequency of 120/n Hz, where n is the number of masses analysed. To distinguish between CO and C$_2$H$_4$ also the ethylene fragmentations at m/e=27 and m/e=26 were measured. Daily calibration of the mass spectrometer was required for obtaining quantitative data.

Generally, a quadrupole mass spectrometer is a very suitable instrument for this type of transient measurements, since it fits all the requirements mentioned in the introduction. The mass resolution of a quadrupole mass spectrometer is, however, too low to distinguish
between isobaric masses such as CO and N₂, as is needed for the study of the kinetics of NO reduction.

2.6. The need for a high resolution mass spectrometer

When studying the kinetics of NO reduction, notably by CO with a quadrupole mass spectrometer, the problem of mass interference arises. The main product from NO reduction is N₂, which has the same mass as CO (m/e = 28 amu). Additionally, a by-product commonly produced by automotive catalysts, is N₂O, which has the same mass as CO₂ (m/e = 44 amu). The latter is present in large quantities up to 14 vol. % in automotive exhaust gases. A solution for this mass interference problem in the quantitative analysis of the product gases could be the use of isotopic gases, e.g. ¹³CO (m/e = 29 amu) or ¹⁵NO (m/e = 31 amu). This solution, however, turns out to be very expensive and non-durable, because gas flow rates are very high in automotive catalysis. One 8-hour day of experiments using 0.5 vol. % ¹³CO requires approximately 0.8 mol or 20 litres (298 K, 100 kPa).

![Peak Profile for Mass 28](image.png)

The mass interference problem for investigating transients in the catalytic reduction of NO by CO is not new. Burch et al. (1998, 1999) as well as Almusaiter & Chuang (1999) and Mergler & Nieuwenhuys (1996) all mention that they cannot measure CO/N₂ and CO₂/N₂O separately, due to the use of a quadrupole mass spectrometer. This makes the interpretation of their data much more complicated. Also Arena et al. (2000) have plotted a combined CO₂/N₂O signal in their transient study of NOₓ storage. Cho (1995) is able to correct for the mass interference at m/e = 28 between N₂ and C₂H₄ by also measuring mass 27 (C₂H₃⁺ fragment). Additionally, experiments with ¹⁵NO were performed. Van Hardeveld et al. (1997) use a very sensitive quadrupole mass spectrometer and in addition to mass 28, also masses 12, 14, 16, and 27 are measured to correct for the mass overlap during their TPD experiments. The results were only used for qualitative interpretation.
Chapter 2

In this work, a durable solution is used for the analysis of the experiments described in Chapters 5 and 6: the high speed of the quadrupole and the mass resolution of the isotopes have been combined by using a high resolution magnetic sector mass spectrometer. Such instrument is able to separate ions on the basis of very small mass differences: CO (m/e = 27.9949 amu), N\textsubscript{2} (m/e = 28.0061 amu) and C\textsubscript{2}H\textsubscript{4} (m/e = 28.0313) as well as CO\textsubscript{2} (m/e = 43.9898 amu) and N\textsubscript{2}O (m/e = 44.0011 amu). Hence, these species can be clearly discriminated, as shown in figure 2.3 for mass 28.

Normally, magnetic sector mass spectrometers are not required to measure at the required sampling rate of approximately 50 Hz. Therefore, hardware and software modifications have been made in order to obtain all the previously mentioned demands (sensitivity, stability, and speed). Furthermore, large differences in gas phase concentrations during the transients require a mass resolution such that two close masses, e.g. CO and N\textsubscript{2}, can be measured without interference even at concentration ratios up to 1:120.

A JEOL JMS-GCMate mass spectrometer, normally used for GC-MS analysis, has been modified and connected to the set-up. This section describes the mass spectrometer, and the adaptation of the data acquisition and processing software.

2.6.1. Hardware description

MS inlet system

In order to study the transient kinetics of the catalyst, it is necessary to prevent mixing of gases in the reactor. This is realised by the plug flow character of the fixed bed reactor, plus the short residence time of the gas in the reactor. The sampling-system, which transfers reactor gas samples toward the analyser, should not affect the time-resolving quality of the reactor, as mentioned before. Therefore the sample inlet of the standard GCMate mass spectrometer had to be modified. The gas-sampling system consists of two capillaries, one at the inlet side of the catalyst bed and one at the outlet side (see Figure 2.1). These capillaries have a length of 1 m, and an inner diameter of 0.13 mm. The small cross section and the high gas flow rate inside the capillaries (at the end of the capillary the flow is even sonic) prevent axial gas dispersion completely (Taylor, 1953). The other ends of the capillaries go to a small-volume 3-way valve (Valco, C3UWE), which is used to direct either the inlet gas or the outlet gas into the analyser (see Figure 2.1).

The capillary-outlet of the 3-way valve is inserted into a much wider glass tube onto its bottom, which consist of a porous glass material with a thickness of 1 mm. The tip of the capillary is adjusted to avoid touching the porous material. The inner diameter of the glass tube is 2.5 mm, and because the outside diameter of the capillary is 0.8 mm, an annular space is present around the capillary, which is evacuated by a vacuum pump. The complete assembly is mounted onto the mass spectrometer so that the porous tip of the glass tube is at a distance of approximately 0.5 mm from the ionisation chamber (see Figure 2.4).

The major part of the sample gas, arriving at the porous end of the glass tube, is removed by the rotary vane vacuum pump, but a small portion passes through the porous plate into the ionisation chamber, where the pressure is of the order of 10^{-4} Pa. The residence time of the gases in the ionisation chamber is small (~0.3 ms), such that the plug flow character of the inlet system is not compromised, and therefore no disruption of the signal takes place. At this
Experimental set-up and equipment

pressure the mean free path length is about 40 m, whereas the dimensions of the ionisation chamber are only of the order of centimetres. Therefore mixing of gases at this point may be considered negligible. As a result of introducing the gases directly into the ionisation chamber, they constitute the principal gases in the chamber, which reduces considerably the residual gas background in the spectra.

The ionisation chamber of the mass spectrometer is at a voltage of approximately 2.5 kV; the metal capillary from the three-way valve to the mass spectrometer is grounded. The use of the glass tube around the capillary makes it possible to "connect" this capillary to the ionisation chamber without short-circuiting the High Voltage power supply. Electrical fields in the ionisation chamber are not influenced by the capillary, since it does not enter the chamber, but remains just outside the chamber wall.

Mass spectrometer system

As described before, a magnetic sector analyser was chosen because of the high mass-resolution requirement. Gas components such as CO, N₂, C₂H₄ have mass differences of about 0.011 amu at about mass 28; this is also the case with CO₂ and N₂O at mass 44. In order to separate the peaks of these gas components, even at high concentration ratios, one needs a resolution of 5,000 (at 20% cut). This resolution can be obtained with a single magnetic sector instrument. For the experiments described in Chapters 5 and 6, a bench-top mass spectrometer JMS-GCmate (JEOL Ltd; Japan) is used. This system incorporates both a magnetic sector and an electrostatic sector. The system is capable to obtain a sufficient resolution for the separation of all components up to at least concentration ratios of 1:120 for CO/N₂.

The system works at an accelerating voltage of 2.5 kV. The ion source and the spectrometer are differentially pumped with turbo molecular pumps to secure clean and high vacuum (10⁻⁴ Pa). With the sensitive photo-multiplier detector, concentrations as low as 30 pg/µl level can be measured. A transmission efficiency of the selected ions of 90% is guaranteed, as a result of the short flight tube (less than 40 cm), and the use of quadrupole lenses to optimise focussing of the beam.

In order to increase the number of measurements per unit of time, it is necessary to use the analyser under SIM (Selected Ion Mode) conditions. Even at this condition, however, one needs to mass-calibrate the instrument after a number of measurements because of drift of the
magnet and/or the accelerating voltage. A good practice would be to calibrate the analyser after each sample measurement. Carrying out this practice, however, caused the effective sampling rate to decrease considerably (more than a factor of two), since "jumping" from the mass calibrate gas (i.e. the lockmass) to the sampling gas requires a certain stabilisation time for both the accelerating voltages for the ions as well as for the magnet. The stability of the analyser was tested by monitoring the peak heights of various single gases (without lockmass) for 5 minutes. During this period, it appeared that the total drift of the system was negligible. Since a typical transient kinetic experiment requires a measuring time of up to 2 minutes for each component in the exhaust gas, the experiment is carried out by mass-calibrating the analyser only in between the measurements of the various components. In this way, it proved possible to assess 48 measurements per second, measuring one single ion in the SIM mode, one component after the other. This avoids the "jumping", and results in a high sampling rate, and simultaneously a low signal/noise ratio because signals are more stable without sudden changes of the electric field.

It turned out that with the high sampling rate both the hardware and the software for the data acquisition were unable to handle the huge data stream. To overcome these hardware limitations, JEOL implemented a HP workstation, including a second interface, to the analyser system. This approach allowed separation of the data acquisition/storage from the mass spectrometer control. Acquisition and storage are carried out by the workstation, while a PC controls the mass spectrometer.

2.6.2. Software description and measurement procedures

The novel combination of experimental apparatus and analytical instrumentation described in this work required both a number of dedicated modifications to the data acquisition software, and the development of special data handling software.

Data Acquisition
The GCMate spectrometer was originally supplied with a PC control and acquisition system, but after installation and testing, it became clear that a sampling frequency of only 25 Hz allowed a total acquisition time of only 45 seconds, before the system overloaded, which was an unacceptably short period. Additionally, the measurements controlled by the PC switched the filament on at the start of the measurement, resulting in a 10 second unstable measurement at the start, reducing the useful measurement time to only 35 seconds. Consequently, the system was upgraded to a Unix based system, which was capable of keeping pace with the fast acquisition rate, and had enough memory to accommodate the large amount of data that were generated during each experiment. In practice, both PC and Unix based systems can operate the instrument, and a switch box selects which system is to be used. The PC system is used for tuning and calibration, and the Unix system for experimental acquisition. Additionally the unstable period of 10 seconds at the start of the data collection is avoided, because the filament has already been turned on by the PC before collection (by the workstation) starts.

Experimental data are collected for each gas component used in the experiment by means of serial measurements via an automatic program. The typical experimental procedure, where regular switches between the reactor feeds are made, allows this. Each measurement of an individual gas component is initiated by the application of an external electronic trigger, from the electromagnetic valves of the reactor set-up. The computer starts measurements
Experimental set-up and equipment

immediately the trigger signal is received. Before the actual measurements start, it is assured that the catalyst is in a stable transient state. Measurements are performed in the Selected Ion Mode (SIM), where one mass is monitored at a sampling rate of 48 Hz. No lock mass is used, since the exact peak position is determined during a separate SIM mass calibration prior to the start of each SIM measurement. Furthermore, noise is reduced during the SIM measurements by scanning over a range of 50-150 ppm (ion dependent) for determining the peak maximum during each measurement of each sample, i.e. 48 times per second. The experimental data per selective ion mass, i.e. absolute time passed after the trigger with corresponding peak intensity as well as exact ion mass, and sampling rate are stored in a data file, and the data is converted to text and exported via the network for processing.

Data Processing

Once the required data sets have been read and loaded, data processing is carried out off-line in four stages, including: Quantitative calibration, Quantification, Correction for fragmentation, Graphical representation. The data processing software, which is completely different from the one that supplied with the standard GCMate, is written in Visual Basic, and runs as a macro within the Microsoft Excel application. The data processing steps are described in detail below.

Quantitative calibration

The macro reads a spreadsheet that contains the names of calibration files with data relating to the concentrations of components used, fragmentation ratios, sampling rate of the measurements, and filenames for the measured inlet and outlet data files. Using this spreadsheet, the macro then determines which files to import for the calculation of the calibration curves, needed for the quantification. The macro imports all calibration files, which provide the exact ion masses and the time-peak intensity relations. A quantification table is then calculated, which contains the average intensity for each gas at its respective concentration. The intensity versus concentration graph (calibration curve) can then be plotted for each gas. Through least squares fitting, the concentrations are related to the measured intensities via a quadratic equation. This gives an accurate fit of the quantitative calibration points. The fitted calibration curves are then used to quantify the data acquired from the experiments.

Quantification

Once the calibration constants have been calculated, the macro reads the acquired experimental data (either inlet or outlet gases at each time). The acquisition cycle has a fixed timing error, which does not cause problems with normal use (e.g. GC-MS or mass scans), but becomes apparent if high sampling frequencies are applied. The necessary time correction to accommodate this effect, is applied automatically to the data, which means that the set sampling time of 20 ms results in reality into a cycle time of 21 ms, corresponding with the indicated 48 Hz. The time correction multiplies all measured times with (21/20). After all raw experimental data has been quantified, correction needs to be made for the fragmentation of certain gases.

Correction for fragmentation

Certain gases, specifically CO₂, NO₂, and C₂H₄, will tend to fragment within the mass spectrometer's ion source, and will therefore contribute to the peak intensities of CO, NO, and C₂H₂. Therefore, correction is necessary. Fragmentation ratios are determined by measuring, for example, both CO and CO₂, when feeding several amounts of CO₂ to the mass spectrometer. The ratios are determined by dividing the CO concentrations by the CO₂
concentrations. The fragmentation ratios are assumed to be concentration independent. Initially, the fragmentation ratios are read from the spreadsheet (fragmentation is considered for NO\textsubscript{2} to NO, CO\textsubscript{2} to CO and C\textsubscript{2}H\textsubscript{4} to C\textsubscript{2}H\textsubscript{2}). Measured concentrations and known fragmentation ratios are substituted into linear equations in order to calculate the actual concentrations.

**Graphical Representation**

The final gas concentrations are graphically represented for each gas by plotting it against the acquisition time in seconds. Each gas is assigned its own colour code to make interpretation of the data easier. The whole process is repeated until all masses have been analysed as a function of time. After both reactor inlet and outlet data have been processed, the macro displays a graph that shows both sets of reactor inlet and outlet data, so that the results can be immediately interpreted to view how concentrations have changed over the catalyst bed.

**2.7. Conclusions**

The experimental set-up described in this chapter provides means for obtaining transient kinetics of fast reactions, involving isobaric masses. It allows two gas mixtures with different compositions to be alternated over a catalytic fixed bed reactor with switching frequencies up to 10 Hz. Also, it allows to perform isothermal experiments under plug flow conditions without significant pressure changes after the switches.

The JEOL magnetic sector mass spectrometer could be used to monitor changes in gas phase concentrations with a sampling frequency of 48 Hz at a mass resolution of 5000 (at 20% cut). This provides sufficient data to monitor 1 Hz oscillations in automotive practice, and the available mass resolution is sufficient to separate CO and N\textsubscript{2} at concentration ratios up to 1:120. N\textsubscript{2}O and CO\textsubscript{2} can also be measured separately. The sensitivity is high enough to measure as low as 0.005 vol. % or lower. The stability is high enough to follow one mass for at least 5 minutes. The signal/noise ratio is sufficiently high in order to distinguish catalytic phenomena from apparatus noise.

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KINETICS OF ETHYLENE OXIDATION OVER Pt/Rh/CeO$_2$/γ-Al$_2$O$_3$

Abstract
The transient kinetics of ethylene oxidation by oxygen over a commercial Pt/Rh/CeO$_2$/γ-Al$_2$O$_3$ three-way catalyst were modelled. Experiments were carried out in a fixed-bed reactor with two separate inlets, enabling alternate feeding of ethylene and oxygen with frequencies up to 1/4 Hz. The experimental conditions resemble the cold-start period of an Otto engine in a car. Two types of adsorbed ethylene species seem to exist. A selective catalyst deactivation for oxygen adsorption, due to deposition of carbonaceous species, was found. A kinetic model was developed, based on elementary reaction steps, that allows to describe the experiments quantitatively. Furthermore, this model was combined with the published model for transient carbon monoxide oxidation over the same catalyst (Nibbelke et al., 1998a), which enables to predict the results of simultaneous ethylene and carbon monoxide oxidation. Both components react in rather distinct zones, ethylene being converted only when carbon monoxide oxidation is almost complete. LEIS experiments have verified the catalyst deactivation, and showed a complete restoration of the Pt surface after exposure to atomic oxygen.

3.1. Introduction

The continuous expansion of road traffic causes an on-going demand for less pollution from automotive engines, which is reflected by more severe legislation. Three-way catalysts allow a simultaneous conversion of hydrocarbons, carbon monoxide, and nitrogen oxides into carbon dioxide, water, and nitrogen, which indeed is very effective at stoichiometric feed conditions, once the catalyst has reached a sufficiently high temperature. At cold start conditions, however, the currently applied converter cannot eliminate all pollutants. The conversion of all pollutants is then completely determined by chemical kinetics.

Therefore, a detailed understanding of the relevant kinetic processes, taking place simultaneously and interactively, is necessary for a further optimisation of the converter. This requires modelling of intrinsic transient kinetics on the basis of elementary reaction steps, because, especially during catalyst warm-up, the operating conditions change continuously, resulting in alterations of the rate-determining step. Moreover, oscillations of the reactor feed composition, as induced by the lambda controller cause transient effects that influence the
time-averaged conversion due to the non-linear character of the kinetics. Using the kinetic model, an optimal motor management system can be developed, which can lead to further reduction of the emissions.

Research at Eindhoven University of Technology aims to produce an elementary step kinetic model, which allows to predict the behaviour of complex exhaust gas mixtures on one type of commercial catalyst, Pt/Rh/CeO$_2$/γ-Al$_2$O$_3$, under transient conditions. Previously, the steady state kinetics of carbon monoxide oxidation (Nibbelke et al., 1997a) and ethylene oxidation (Nibbelke et al., 1997b) as well as the transient kinetics of carbon monoxide oxidation (Nibbelke et al., 1998a) have been reported for this catalyst.

In this study, ethylene was chosen as representative for many different hydrocarbons in an automotive exhaust gas, notably hydrocarbons, which are easily oxidised. According to Impens (1987), most abundant hydrocarbons are typically ethylene (25 mol% of the total hydrocarbons), acetylene and methane (both 20 mol%), and aromatics (toluene: 15 mol%, and benzene 5 mol%). Ethylene has been shown to display similar oxidation behaviour as toluene and benzene (Mabilon et al., 1995; Bart et al., 1992).

From steady state studies on alkene oxidation around the stoichiometric point, usually a negative partial reaction order for the alkene and a positive order for oxygen was found with Pt and Pd catalysts (Cant & Hall, 1970; Voltz et al., 1973; Hawkins & Wanke, 1979; Yao, 1984; Shinjoh et al., 1989), while only under a large excess of oxygen these orders are reversed (van de Beld et al., 1994; Vayenas et al., 1980). For Rh catalysts a negative partial reaction order for oxygen and a positive order for ethylene was found (Cant & Hall, 1970; Yao, 1984; Shinjoh et al., 1989). Burch and Watling (1997) studied the steady state oxidation of propane and propene in the presence of nitrogen oxide and excess oxygen over Pt/Al$_2$O$_3$ catalyst. For propene they concluded that the catalytic surface was predominantly covered with hydrocarbon species, while for propane, the surface was mainly covered by oxygen adatoms. Work by Voltz et al. (1973) for carbon monoxide and propene oxidation by oxygen and nitrogen oxide over Pt/Al$_2$O$_3$, and by Montreuil et al. (1992) for propane and propene oxidation over a Pt/Rh catalyst show inhibition by hydrocarbons and CO.

Several transient studies were performed on the influence of the oscillation frequency on hydrocarbons oxidation. The oscillation frequency for maximum conversion of propene over Pt, Pd and Rh increased with increasing oscillation amplitude and temperature (Muraki et al., 1985), but a decrease with increasing temperature was reported as well for the oxidation of propene and propane (Shinjoh et al., 1989). Light-off of C1 to C9 hydrocarbons decreases due to feed cycling, because of less hydrocarbon inhibition (Amon-Meziere et al., 1995; Silveston, 1995).

Sant & Wolf (1989) constructed a kinetic model, based on elementary reaction steps, for the transient oxidation of ethylene over a Pt/SiO$_2$ catalyst. It contains two separate pathways, one leading directly to CO$_2$ under oxygen rich conditions and one with CO as an intermediate product for oxygen poor conditions.

The influence of ceria on the oxidation of hydrocarbons is said to be negligible or negative below 573 K (Padeste & Baiker, 1994; Diwell et al., 1991; Wittington et al., 1995), but above 573 K ceria may enhance hydrocarbon oxidation (Trovarelli, 1996) by supplying oxygen. This chapter presents results from experiments and kinetic modelling for the transient oxidation of ethylene, and for the transient oxidation of ethylene and carbon monoxide.
mixtures. This model is based on elementary reaction steps, and includes earlier work (Nibbelke et al., 1998a) on carbon monoxide oxidation over the same catalyst. Typical experimental conditions refer to automotive catalysis.

3.2. Experimental

The experimental set-up, used for the transient oxidation of ethylene and carbon monoxide via cyclic feeding, has been described in detail in Chapter 2. Analysis was performed with online quadrupole mass spectrometry (VG Sensorlab 200D) for steady state and transient measurements. MS analysis was done with a frequency of 120/n Hz, with n the number of masses analysed. To distinguish between CO and C2H4, the ethylene fragmentations at m/e=27 and m/e=26 were measured. In such case, analysis was performed on masses 4 (He), 26 (C2H4), 27 (C2H4), 28 (CO+CO2+C2H4), 32 (O2), and 44 (CO2). Water was not measured. The range of the experimental conditions is depicted in table 3.1.

3.3. Experimental results and discussion

Two types of cyclic feeding experiments have been carried out: 1) experiments with one feed of ethylene in helium and a second feed of oxygen in helium, and 2) experiments, like type 1), but with carbon monoxide added to the ethylene in helium feed.

The time-averaged ethylene conversion increased with increasing temperature and oscillation frequency for the investigated conditions (see table 3.1), which is in line with literature sources (Muraki et al., 1985; Silveston, 1995). An optimal duty cycle was found at 50% (at 423K, 1/10 Hz). CO was not observable during type 1 experiments, which differs from reported results over a Pt/SiO2 catalyst (Sant & Wolf, 1989). Any significant influence from ceria could be excluded, since similar results as on the commercial catalyst were obtained with a model Pt/γ-Al2O3 catalyst. This is in line with reported results (Padeste & Baiker, 1994; Diwell et al., 1991; Whittington et al., 1995). The catalytic activity of ceria at the used temperatures has been excluded (Nibbelke et al., 1997b).

An inlet signal at a frequency of 1/10 Hz is shown in figure 3.1a. Figure 3.2a shows an inlet signal with 0.1 kPa carbon monoxide added to the ethylene in helium flow. At the applied total flow rate, a step change is completed in 0.3 s. The corresponding outlet signals at a temperature of 423 K can be seen in figures 3.1b and 3.2b for the reactants, and in figures 3.1c and 3.2c for the reaction products. Both experimental data (markers) and model predictions (curves) are shown. The latter will be discussed later.

<table>
<thead>
<tr>
<th>Table 3.1, Range of experimental conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature K</td>
</tr>
<tr>
<td>total pressure kPa</td>
</tr>
<tr>
<td>( p_0 \text{ C}_2\text{H}_4 ) kPa</td>
</tr>
<tr>
<td>( p_0 \text{ O}_2 ) kPa</td>
</tr>
<tr>
<td>( p_0 \text{ CO} ) kPa</td>
</tr>
<tr>
<td>frequency Hz</td>
</tr>
<tr>
<td>duty cycle %</td>
</tr>
<tr>
<td>( W_{\text{cat}} ) 10^-3 kg\text{cat}</td>
</tr>
<tr>
<td>cat dilution ( m_3^\text{inert} )</td>
</tr>
<tr>
<td>( m_3^\text{inert+cat} )</td>
</tr>
<tr>
<td>total flow mol s^-1</td>
</tr>
</tbody>
</table>
Chapter 3

Figure 3.1. a. Measured reactor inlet concentrations of oxygen and ethylene versus time at an oscillation frequency of 1/10 Hz.
b. Reactor outlet concentrations of oxygen and ethylene (markers: measured; lines: model predictions) versus time at a temperature of 423 K and an oscillation frequency of 1/10 Hz.
c. Reactor outlet concentrations of carbon dioxide (markers: measured; lines: model predictions) versus time at a temperature of 423 K and an oscillation frequency of 1/10 Hz. (Note the different vertical scale)

Figure 3.2. a. Measured reactor inlet concentrations of oxygen, carbon monoxide, and ethylene versus time at an oscillation frequency of 1/10 Hz.
b. Reactor outlet concentrations of oxygen, carbon monoxide, and ethylene (markers: measured; lines: model predictions) versus time at a temperature of 423 K and an oscillation frequency of 1/10 Hz.
c. Reactor outlet concentrations of carbon dioxide (markers: measured; lines: model predictions) and water (model predictions) versus time at a temperature of 423 K and an oscillation frequency of 1/10 Hz. The dotted vertical line indicates the time value that applies for figures 3.5 and 3.6.
d. Detail of the experiment and model prediction between $t = 6$ and $t = 12$ s.
At this low frequency of 1/10 Hz, the concentrations of ethylene and oxygen when fed to the reactor, slowly relax towards the corresponding inlet levels, see figure 3.1b, indicating the consumption of the reactants by surface species that were adsorbed during the previous half-cycle. When switched off, the outlet concentrations of oxygen and ethylene immediately decrease to zero, meaning that significant reversible adsorption onto the ceria or the alumina carrier can be excluded.

When switching from ethylene to oxygen (e.g. at time = 10 s) a peak of CO\(_2\) arises in the outlet signal, corresponding to the amount of ethylene adsorbed on the catalyst surface, right before switching. This peak consists of a very steep ascent, and a slower descend, that abruptly retards, at about 12 s, before decreasing to zero. This indicates the presence of two types of ethylene surface species, one which is oxidised very fast, and a second, which is oxidised much slower. It is reasonable to assume that the second type of species can be formed from the first, using vacant sites that arise at the catalytic surface. The fast reacting species is ascribed to \(\pi\) ethylene, adsorbed on one single active site, while the slow reacting, more stable species would be \(\text{di-}\sigma\) ethylene, adsorbed on two noble metal sites (Paul et al., 1994; Mohsin et al., 1988; Berlowitz et al., 1985; Velic & Levis, 1996; Szulczewski & Levis, 1996). The CO\(_2\) peak at the switch from oxygen to ethylene (e.g. at time = 6 s) corresponds with adsorbed O adatoms on the catalyst. The peak has a much smaller surface area, which is partly due to stoichiometry. Therefore, all oxygen on the surface will be consumed very rapidly by the adsorbing ethylene.

When comparing the ethylene-only-oxidation with an experiment where carbon monoxide is added to the ethylene containing feed, figures 3.2b and 3.2c show that the oxidation of ethylene becomes inhibited, resulting in a faster relaxation of the ethylene outlet signal and in larger CO\(_2\) peak areas. Contrary to carbon monoxide, ethylene is unable to adsorb significantly on an oxygen covered site, resulting in an immediate break-through of the ethylene signal (time = 7 s), while the CO signal shows a considerable lag time (about 1.5 s). The ethylene outlet concentration may even exceed temporarily its inlet concentration. Applying higher CO partial pressures than 0.1 kPa, leads to a strong increase of the inhibition, until hardly any ethylene is converted at a CO partial pressure of 0.3 kPa. Clearly, CO adsorbs faster onto the noble metal, blocking sites for ethylene.

The increased peak area of the CO\(_2\) peak at 2-3 s in figure 3.2c, when compared to figure 3.1c is due to stoichiometry and the presence of the bifunctional ceria path for CO oxidation (Nibbelke et al., 1998a; Nibbelke et al. 1997b). The shape of the small CO\(_2\) peak in figure 3.2c is however completely different from the experiments with CO only, which could indicate that the CO oxidation becomes inhibited by refractory \(\text{di-}\sigma\) ethylene. Like in the CO only oxidation (Nibbelke et al., 1998a), the direct adsorption of CO on an oxygen-covered site is the main path here, resulting in a long period of 100% CO conversion. The vacant sites, which are formed that way, will partly become occupied by ethylene, which retards the reaction between adsorbed CO and adsorbed oxygen. This, and reaction stoichiometry, results in a smaller CO\(_2\) peak then in the CO-only-oxidation. From the slow relaxation of the CO signal towards the inlet level, it can be concluded that the tail of the CO\(_2\) peak is mainly due to CO oxidation, resulting in a surface which is primarily covered with CO.

The large carbon dioxide peak in figure 3.2c, (at 2-3 s) when switching from rich to lean, displays the same type of behaviour as in the ethylene-only-oxidation, (figure 3.1c) however the peak is much higher and the tail is narrower, as \(\text{di-}\sigma\) ethylene is largely inhibited by the abundant presence of CO* on the noble metal surface. The corresponding oxygen signal in
Chapter 3

Figure 3.2b supports this point, since around 2 s it shows a temporary decrease, which is typical for transient CO oxidation (Nibbelke et al., 1998a). This temporary decrease is much more pronounced than for ethylene-only-oxidation, see figure 3.1b, which shows only a small retardation of the oxygen concentration rise.

3.4. Kinetic modelling of the ethylene oxidation

The transient kinetic responses have been modelled in a similar way as described by Nibbelke et al. (Nibbelke et al., 1998a) The essentials are summarised below. The objective of the modelling work is to construct a transient kinetic model, which allows to give an adequate description of the measured C₂H₄, O₂, and CO₂ concentrations at the reactor outlet with a given inlet in time.

3.4.1. Reactor model equations

The fixed-bed micro reactor is regarded as an ideal isothermal plug flow reactor, with a constant total molar flow rate along the catalyst bed. The model consists of the continuity equations for

1) C₂H₄, O₂, and CO₂ in the gas phase,
2a) the surface species adsorbed on the noble metal surface,
2b) the CO₂ adsorbed on the γ-Al₂O₃ support.

Adsorption on ceria was excluded because of experimental evidence, see the previous section.

The continuity equation for gas phase component i is as follows:

$$\frac{\partial C_i}{\partial t} + \frac{1}{\tau} \frac{\partial C_i}{\partial z} = \frac{\rho_i}{\varepsilon_i} \sum_k L_k R_{k,i}$$ (3.1)

The continuity equations for species j adsorbed on the noble metal surface, and species n adsorbed on the support surface, can be written as follows:

$$\sum_k L_{NM} \frac{\partial \theta_{k,j}}{\partial t} = \sum_k L_k R_{k,j}$$ (3.2a)  
$$\sum_k L_{SUP} \frac{\partial \delta_{k,n}}{\partial t} = \sum_k L_k R_{k,n}$$ (3.2b)

As the initial condition for Equations (3.1) and (3.2), the steady solution corresponding to the experimental conditions during the rich feeding half cycle, i.e. 0.15 mol% C₂H₄ (plus 0.1 mol% CO if relevant) in helium at reaction temperature, was chosen.

The boundary condition for Equation (3.1) is as follows:

$$z = 0, \ t > 0, \ C_i = C_i^0(t)$$ (3.3)

The experimentally measured reactor inlet concentrations were used to produce model predictions for the outlet responses. The reactor inlet concentrations of CO₂ and H₂O were always kept zero.

The production rates in Equations (3.1) and (3.2) can be calculated from the rates of the elementary reaction steps in the reaction mechanism, which is considered in section 3.4.4.: 

$$R_{k,j} = \sum_p v_{i,p} r_{k,p}$$ (3.4)

The reaction rates r_{k,p} of the elementary reaction steps are calculated via the law of mass action. The adsorption capacity is restricted to a monolayer as maximum.
Since the calculations started from the steady state solution as initial condition, they had to be carried out until a stable periodic solution was reached. The latter was usually the case after one half cycling period.

3.4.2. Numerical calculations

A backward differentiation formula, BDF, integrator from the NAG Fortran library [Mark 18, 1997] (NAG, 1997), routine D02NHF, was used for calculating the steady state solution of Equations (3.1) and (3.2).

The transient calculations were carried out using the Method of Lines (Velic & Levis, 1996). This method consists of discretisation of the space-derivatives by finite differences. The set of partial differential equations becomes a set of ordinary differential equations, ODE, which can be integrated in time by an ODE integrator. The first order space-derivatives, i.e. the convection terms in Equation (3.1), were discretised by so-called backward or upstream differentiation. The time-integration was carried out using a BDF integrator from the NAG Fortran library (NAG, 1997), routine D02NCF. The numerical calculations were carried out on a Silicon Graphics CRAY Origin2000. A typical CPU time for simulating two periods amounts 80 s.

3.4.3. Regression analysis

Estimation of the kinetic parameters was performed with non-linear multi-response regression analysis of the C\textsubscript{2}H\textsubscript{4}, O\textsubscript{2}, and CO\textsubscript{2} outlet concentrations. The following objective function was minimised:

\[ S(b) = \sum_{l=1}^{v} \sum_{i=1}^{n} w_{l,i} [y_{i,l} - g_{q}(x_{l}, b)]^2 \rightarrow \text{minimum} \]  \hspace{1cm} (3.5)

The symbols are explained in the section ‘Nomenclature’ of this thesis. The function represents the weighted sum of squares for all measured gas phase concentrations over the entire experimental time, except for the first, unstable, cycle. Minimisation was achieved with a multi-response Levenberg-Marquart algorithm (Froment & Hosten, 1981; Boggs et al., 1992). The regression of the transient ethylene oxidation, was carried out for experiments at frequencies of 1/4, 1/6 and 1/10 Hz at temperatures of 393, 423 and 443 K, leading to nine independent data sets with a total of 8916 experimental data points. All weight factors were set to unity. The assessment of the confidence intervals for the individual rate parameters is not trivial. Appendix 6B addresses this problem for the regression results from Chapters 3, 4 and 5.

In practice, the regression process for determining the kinetic rate parameters is not straightforward. Regression may often not lead to the minimum sum of squares, but will end in a local minimum of the sum of squares space. This is due to the high non-linearity of the model. Therefore, additional means are necessary in order to verify the adequacy of the model prediction. The most important criterion for this is the ability of the model to predict the most important experimental phenomena both qualitatively and quantitatively. This can only be verified by means of visual inspection. Another method, used solving the problem of the local minima, is the application of a so-called ‘random search engine’. Such engine will change indicated rate parameters, by multiplying these with a random factor (usually between 0.1 and 9) whereupon the new sum of squares is determined. If a lower sum of squares is obtained, then a regression is started. If a higher sum of squares is obtained, as is most often
the case, the parameters are randomly changed again. It may be clear that the ‘random search method’ requires large amounts of calculation time. When no sum of square reduction is obtained after several attempts, it is assumed that the absolute minimum has been found. If, upon visual inspection, the model prediction is rejected, then it is assumed that the underlying model was unable to give an adequate prediction of the experiments, and therefore had to be changed.

The estimation of confidence intervals for each kinetic parameters in not trivial, since measured data points are dependant. This issue is addressed in Appendix B of Chapter 6.

3.4.4. Reaction mechanism

On the basis of the experimental results, a reaction scheme is suggested for the oxidation of ethylene, see table 3.2.

The adsorption of oxygen (step 1) has been taken the same as in the published model for CO oxidation (Nibbelke et al., 1998a) for compatibility reasons and is first order in the fraction of vacant sites (Nibbelke et al., 1997a). A very slow desorption step ($k_1 = 1.10^{-10} \text{s}^{-1}$) has been included for numerical stability only (Nibbelke et al., 1998b), since actual oxygen desorption is negligible at the investigated conditions (Engel & Ertl, 1979). The reversible adsorption of ethylene (step 2) leads to refractory di-\(\sigma\) ethylene on the surface and is second order in the vacant sites.

Attempts to model the ethylene adsorption to form directly \(\pi\) ethylene did not lead to a satisfactory prediction of the experimental data. Although significant ethylene desorption was not detected during the experiments, ethylene is likely to desorb to some extent (Nibbelke et al., 1997b; Sant & Wolf, 1989), creating vacant sites for oxygen adsorption, especially after a switch from rich to lean. It is clear that the desorption coefficient should be low at the temperatures considered. Step 3 describes the reversible conversion of the two types of adsorbed ethylene into each other.

The conversion of di-\(\sigma\) ethylene to \(\pi\) ethylene yields a vacant site, making the latter species more abundant when ethylene is in the gas phase (rich period). However, this will take time, since adsorption of ethylene at first leads to di-\(\sigma\) ethylene. The direct and total combustion of both ethylene species is described by steps 4 and 5, i.e. reaction paths A and B. Although not elementary, the first and rate determining step is assumed to be the oxygen assisted abstraction of the first hydrogen atom, whereupon total combustion occurs instantaneously (Nibbelke et al., 1997b). The massive decomposition of ethylene on the surface was excluded, because Temperature Programmed Desorption (TPD) experiments with a used catalyst showed considerable amounts of ethylene, desorbing at temperatures above 573 K. Steps 6 and 7 show an Eley-Rideal type of reaction path (path C) for the combustion of ethylene. This is needed to initiate ethylene adsorption onto a surface, fully covered by oxygen. As it is not responsible for a significant ethylene conversion, the rate constants are expected to be low. The parameters of the reverse reaction of step 6 were set in advance on low values for numerical stability reasons only (Nibbelke et al., 1998b). Step 8, finally, describes the reversible adsorption of carbon dioxide on the alumina support of the catalyst. This step has been taken directly from Nibbelke et al. (1998a).
Table 3.2. Elementary steps considered in the kinetic modelling of the transient ethylene oxidation by oxygen over Pt/Rh/CeO$_2$/γ-Al$_2$O$_3$.

<table>
<thead>
<tr>
<th>Step no.</th>
<th>Elementary reaction step</th>
<th>Reaction path</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>O$_2$(g) + 2*</td>
<td>$k_1^f$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_1^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_2^f$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2O*</td>
</tr>
<tr>
<td>2</td>
<td>C$_2$H$_4$ (g) + 2*</td>
<td>$k_2^f$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_2^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C$_2$H$_4$$^*$</td>
</tr>
<tr>
<td>3</td>
<td>C$_2$H$_4$$^*$</td>
<td>$k_3^f$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_3^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C$_2$H$_4$$^<em>$$^</em>$</td>
</tr>
<tr>
<td>4</td>
<td>C$_2$H$_4$$^<em>$$^</em>$ + 6O*</td>
<td>$k_4^f$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2CO$_2$ + 2H$_2$O + 8*</td>
</tr>
<tr>
<td>5</td>
<td>C$_2$H$_4$$^<em>$ + 6O</em></td>
<td>$k_5^f$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_5^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2CO$_2$ + 2H$_2$O + 7*</td>
</tr>
<tr>
<td>6</td>
<td>C$_2$H$_4$ (g) + O*</td>
<td>$k_6^f$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_6^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C$_2$H$_4$O*</td>
</tr>
<tr>
<td>7</td>
<td>C$_2$H$_4$O* + 5O*</td>
<td>$k_7^f$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_7^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2CO$_2$ + 2H$_2$O + 7*</td>
</tr>
<tr>
<td>8</td>
<td>CO$_2$ (g) + $\gamma$</td>
<td>$k_8^f$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_8^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CO$_2$$\gamma$</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_4$ + 3 O$_2$</td>
<td>$k_9^f$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_9^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2CO$_2$ + 2H$_2$O</td>
</tr>
</tbody>
</table>

3.4.5. Selective deactivation

During the modelling work, it appeared impossible to explain just by stoichiometry the difference between the large CO$_2$ peak, when switching from ethylene to oxygen, and the small CO$_2$ peak, when switching from oxygen to ethylene. Applying the current model and several variations always yielded a smaller ratio between the large and the small CO$_2$ peak area, than was measured during the experiments. Apparently the catalyst’s sorption capacity for ethylene is larger than for oxygen. As a ceria contribution could be excluded for the reaction between ethylene and oxygen at temperatures below 500 K, the noble metal sorption capacity was assumed to be different for both reactants. A selective deactivation for oxygen was included in the model, leading to a maximum fractional oxygen coverage that is lower than one. A possible physical explanation for this selective deactivation could be the
deposition of carbonaceous species from ethylene, which do not participate in the reaction, but which block vacant sites for oxygen adsorption, whereas ethylene is insensitive for this kind of deposition.

Indeed, deposition of carbonaceous species and hydrocarbon fragments from ethylene is known to cause deactivation (Berlowitz et al., 1985; Kvon et al., 1997; Kvon et al., 1998; Kepinski, 1999). In the present case, experimental evidence was obtained from elemental analysis, which showed that the used catalyst contained 1.5 mass % carbon. This deposition took place within a few hours time-on-stream, while afterwards the catalyst showed, from MS analysis, a stable activity for at least three weeks. Temperature Programmed Desorption experiments showed, besides large quantities of ethylene, the presence of higher hydrocarbons and Temperature Programmed Oxidation showed two CO2 peaks at 450 K and 850 K. The CO2 from the peak at 850 K emerges from carbonaceous species, which will have become refractory towards oxidation during the experiments.

Chemisorption experiments, done with ethylene and oxygen were not conclusive with respect to the available noble metal surface, as they were hindered by the presence of ceria in the catalyst. Often however, they showed extremely large dispersions for ethylene. Characterisation with LEIS (Low Energy Ion Scattering; Cortenraad et al., 1999) showed that the platinum surface area of the used catalyst was reduced by 50% in comparison to the fresh catalyst. More details are reported in section 3.7. Recently, carbon deposition around noble metal particles from exposure to CO was reported for Pt/CeO2 and Rh/CeO2 catalysts (Bernal et al., 1999). Such phenomenon was not observed during the earlier work (Nibbelke et al., 1998a) on CO oxidation over the present catalyst, which could be ascribed to the lower temperatures used.

For the current modelling work, carbonaceous layers were introduced in the model equations, described as a fraction of the noble metal capacity, which is not accessible for oxygen only. The rate constants for ethylene adsorption and reaction on the carbonaceous species were assumed to be the same as on the noble metal. Furthermore, the carbonaceous species were assumed to be equally distributed over the entire noble metal surface.

3.4.6. Kinetic model equations

The fractions of vacant sites on the noble metal and on the carbonaceous species are defined as:

\[ \theta_s = 1 - \theta_O - \theta_{C,H,s} - \theta_{C,H,s} - \theta_{C,H,O} - \theta_{CH} \]

\[ \theta_C = \theta_{CH} - \theta_{C,H,s} - \theta_{C,H,s} \]

(3.6)

(3.7)

All fractions \( \theta \) are defined as number of sites, relative to the total number of metal sites. The production rates for the gas phase components in equation (3.1) become:

\[ \sum_k L_k R_{k,O_2} = L_{NM} \left( -k_f^{i} C_{O_2} \theta_s + k_b^{i} \theta_O \right) \]

(3.8)

\[ \sum_k L_k R_{k,C,H_4} = L_{NM} \left( -k_2^{C} C_{H_4} \left( \theta_s^2 + \theta_C^2 \right) + k_5^{C} \left( \theta_{C,H,s} + \theta_{C,H,s} \right) - k_4^{C} C_{C,H_4} \theta_{O} + k_8^{C} \theta_{C,H,O} \right) \]

(3.9)

\[ \sum_k L_k R_{k,CO_2} = L_{NM} \left( 2k_5^{C} \left( \theta_{C,H,s} + \theta_{C,H,s} \right) \theta_O + 2k_3^{C} \left( \theta_{C,H,s} + \theta_{C,H,s} \right) \theta_O + 2k_4^{C} C_{C,H_4} \theta_{O} \right) \]

\[ + L_{SUP} \left( -k_f^{i} C_{CO_2} \delta_s + k_b^{i} \delta_{CO_2} \right) \]

(3.10)
\[ \sum_{k} L_k R_{k,H,O} = L_{NM} \left( 2k_5^f \left( \theta_{C_{2}H_{4}^{**}} + \theta_{C_{2}H_{4}^{**}} \right) \theta_O + 2k_5^f \left( \theta_{C_{2}H_{4}^{**}} + \theta_{C_{2}H_{4}^{**}} \right) \theta_O + 2k_5^f \theta_{C_{2}H_{4}O} \theta_O \right) \] (3.11)

The production rates of the noble metal surface species for insertion into equation (3.2) are written as:

\[ \sum_{k} L_k R_{k,O^{**}} = L_{NM} \left( 2k_5^f \theta_{C_{2}H_{4}^{**}} - 2k_5^b \theta_O - 6k_5^f \left( \theta_{C_{2}H_{4}^{**}} + \theta_{C_{2}H_{4}^{**}} \right) \theta_O - 6k_5^f \left( \theta_{C_{2}H_{4}^{**}} + \theta_{C_{2}H_{4}^{**}} \right) \theta_O \right) \] (3.12)

\[ \sum_{k} L_k R_{k,C_{2}H_{4}} = L_{NM} \left( 2k_5^f \theta_{C_{2}H_{4}^{**}} - 2k_5^b \theta_{C_{2}H_{4}}^{**} - 2k_5^f \theta_{C_{2}H_{4}}^{**} + 2k_5^b \theta_{C_{2}H_{4}}^{**} \theta_O - 2k_5^f \theta_{C_{2}H_{4}}^{**} \theta_O \right) \] (3.13)

\[ \sum_{k} L_k R_{k,C_{2}H_{2}^{**}} = L_{NM} \left( k_6^f \theta_{C_{2}H_{2}}^{**} - k_6^b \theta_{C_{2}H_{2}O} - k_6^f \theta_{C_{2}H_{2}O} \theta_O \right) \] (3.14)

\[ \sum_{k} L_k R_{k,C_{2}H_{2}} = L_{NM} \left( k_6^f \theta_{C_{2}H_{2}^{**}} - k_6^b \theta_{C_{2}H_{2}}^{**} \theta_O - k_6^f \theta_{C_{2}H_{2}}^{**} \theta_O \right) \] (3.15)

\[ \sum_{k} L_k R_{k,C_{2}H_{2}O} = L_{NM} \left( 2k_5^f \theta_{C_{2}H_{2}^{**}} \theta_O - 2k_5^f \theta_{C_{2}H_{2}^{**}} - 2k_5^f \theta_{C_{2}H_{2}^{**}} \theta_O + 2k_5^b \theta_{C_{2}H_{2}}^{**} \theta_O - 2k_5^f \theta_{C_{2}H_{2}^{**}} \theta_O \right) \] (3.16)

\[ \sum_{k} L_k R_{k,C_{2}H_{2}^{**}} = L_{NM} \left( 2k_5^f \theta_{C_{2}H_{2}^{**}} - 2k_5^f \theta_{C_{2}H_{2}^{**}} - 2k_5^f \theta_{C_{2}H_{2}^{**}} \theta_O + 2k_5^b \theta_{C_{2}H_{2}}^{**} \theta_O - 2k_5^f \theta_{C_{2}H_{2}^{**}} \theta_O \right) \] (3.17)

The production rate of CO2 adsorbed on the support sites \( \gamma \) becomes:

\[ \sum_{k} L_k R_{k,CO_{2}^{**}} = L_{SUP} \left( k_{8}^f \delta_{CO_{2}}^{**} - k_{8}^b \delta_{CO_{2}} \right) \] (3.18)

Generally, adsorption steps were taken as not temperature dependent, whereas surface reactions and desorption steps were correlated with temperature through an Arrhenius type of equation:

\[ k_i = A_i \exp\left(-\frac{E_{a,i}}{RT}\right) \] (3.19)

The kinetic parameters of steps 1 and 8 and the catalyst properties, including the CO2 sorption capacity of the support, were taken from the model of the transient CO oxidation for the same catalyst (Nibbelke et al., 1998a). The noble metal capacity was determined from CO chemisorption on a used catalyst as 6.3 mmol sites kgcat\(^{-1}\), and the support capacity was taken from previous experiments (Hoebink et al., 1999). All other rate parameters, e.g. activation energies and pre-exponential factors, were determined by regression.

For the model used to describe the combined ethylene and carbon monoxide oxidation, the equations from the CO-only-oxidation (Nibbelke et al., 1998a) have been added to the ethylene model. This involves also mass balances for oxygen adsorbed on ceria. Furthermore, an adjustment to equation (3.10) has been made for the consumption of oxygen atoms on the noble metal surface by adsorbed CO. It was found that the capacities of the noble metal and ceria had to be changed in order to describe the experiments adequately. This was done by regression. Rate parameters, however, were not changed, but kept equal to the current values for ethylene oxidation, and previous values (Nibbelke et al., 1998a) for CO oxidation.
3.5. Modelling results and discussion of the ethylene oxidation

3.5.1 Comparison of model predictions and experiments

The kinetic parameters, as determined from non-linear regression, are listed in table 3.3. The $\theta_{\text{CH}_x}$ indicates the fraction of noble metal sites, which are covered by carbonaceous deposits, as explained in section 3.4.5. The model predictions at a temperature of 423 K and a frequency of 1/10 Hz can be seen as drawn curves in figures 3.1b and 3.1c. In general, the model gives a good prediction of the experimental data. A small oxygen breakthrough peak ($t = 11$ s), predicted by the model, is not observed during the experiment. At that time, however, the measured oxygen signal displays a first deviation from the inlet signal, indicating that the oxygen consumption becomes significant. The modelled CO$_2$ signals are somewhat retarded compared to the measurements, which could be due to a lower CO$_2$ adsorption capacity of the carrier, than used in the model. Deposition of carbonaceous species onto the alumina carrier could explain such an effect.

At higher temperatures, a larger CO$_2$ peak was observed, when switching from lean to rich, whereas the CO$_2$ peak at the switch from rich to lean remained the same. This is explained by the model, which predicts higher C$_2$H$_4^*$ / C$_2$H$_4^{**}$ ratios on the noble metal surface at higher temperatures.

3.5.2. Model parameter comparison

A comparison between the currently regressed rate parameters and previously reported rate parameters is being made. It should be realised, however, that comparing rate parameters obtained from different catalysts may not always be relevant (Nibbelke et al., 1998a). Especially comparison between parameters derived from steady state studies and parameters, derived from transient studies is difficult because of possibly non-uniform fractional coverages occurring under transient conditions.

The parameters for steps 1 and 8 in table 3.2 have been compared elsewhere with literature sources (Nibbelke et al., 1998a; Nibbelke et al., 1997b). Several authors reported sticking coefficients for ethylene adsorption. Sant and Wolf (1989) reported a sticking coefficient of 0.35, while Fischer and Kelemen (1977) reported values between 0.2 and 0.5. If recalculated, the currently found adsorption coefficient would give a sticking coefficient of 0.4, which is close to the literature values. The frequency factor for the desorption of ethylene, as reported by Sant and Wolf, equals $6.5 \times 10^{13}$ s$^{-1}$, whereas Berlowitz et al. (1985) reported a value of $1.0 \times 10^{13}$ s$^{-1}$. The current value of $3.3 \times 10^9$ s$^{-1}$ is much lower, leading to a lower desorption coefficient. The activation energy of 75 kJ/mol for di-$\sigma$ ethylene falls within the expected range: Sant and Wolf (1989): 115 kJ/mol; Berlowitz et al. (1985) 57 kJ/mol; Nibbelke et al. (1997b) 172 kJ/mol; Yeo et al. (1996) 70-184 kJ/mol. The high values of 172 and 184 kJ/mol concern catalyst surfaces with many vacant sites, while the value of 70 kJ/mol was reported by Yeo et al. (1996) for an almost fully covered surface.

For step 3, a comparison is not possible, as such steps were not reported previously. The pre-exponential factors are quite low, compared with values predicted by transition state theory (Zhdanov, 1998). Steps 4 and 5 describe the combustion of the adsorbed ethylene species. Comparison of the rate parameters is hindered by the involvement of two types of adsorbed ethylene. For di-$\sigma$ ethylene, Sant and Wolf reported a value of $8.0 \times 10^7$ s$^{-1}$ for the pre-exponential factor and an activation energy of 54 kJ/mol. Cant and Hall (1970) published
values of respectively $2.1 \times 10^8$ s$^{-1}$ and 77 kJ/mol. In the current work, values of $3.5 \times 10^2$ s$^{-1}$ and 11 kJ/mol were found for $\pi$ ethylene, while for di-$\sigma$ ethylene values of $1 \times 10^{10}$ s$^{-1}$ and 254 kJ/mol were found, which indicate the difference in reactivity for both species. The parameters of step 6 are within the range expected for molecular adsorption, while for step 7, the activation energy is in between the values for oxidation of $\pi$ and di-$\sigma$ ethylene.

Table 3.3. Estimates of the kinetic rate parameters obtained by regression of the cyclic feeding experiments at three temperatures, i.e. 393, 423, 443 K, and forcing frequencies of 1/4, 1/6 and 1/10 Hz for the ethylene oxidation by oxygen over Pt/Rh/CeO$_2$/γ-Al$_2$O$_3$. The parameters with $^*$ are taken from Nibbelke et al. (1998a) The parameters with # are set to low values for numerical stability only (Nibbelke et al., 1998b). Dimensions $k$: m$^3$/mol/s, $A$: s$^{-1}$, $E$: kJ/mol

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_1$</td>
<td>$1.00 \times 10^{10}$</td>
</tr>
<tr>
<td>$k_2$</td>
<td>$1.26 \times 10^6$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$3.33 \times 10^9$</td>
</tr>
<tr>
<td>$E_2$</td>
<td>75.5</td>
</tr>
<tr>
<td>$A_3$</td>
<td>$1.39 \times 10^9$</td>
</tr>
</tbody>
</table>

3.5.3. Fractional coverages during ethylene oxidation

It should be noted that in all figures, the degree of coverage for ethylene species is always the sum of ethylene coverages on noble metal and on carbonaceous deposits.

Model predicted fractional surface coverages at the reactor outlet are displayed in figure 3.3 for the same conditions that apply to figure 3.1. Due to carbon deposition the maximum attainable coverage with O adatoms is around 0.34. Upon switching from oxygen to ethylene, at $t = 6$ s, the latter rapidly adsorbs onto the noble metal surface, at first through the Eley-Rideal path, which leads to immediate CO$_2$ production (figure 3.1b, c), and thereafter mainly as di-$\sigma$ ethylene. It can be seen that the Eley-Rideal species does not play a large role as a surface species, as it does not reach high fractional surface coverages. However, modelling without this path did not yield a satisfactory description of experiments. The di-$\sigma$ ethylene is quickly transformed to the reactive $\pi$ ethylene, which removes oxygen adatoms from the surface. As the oxidation of $\pi$ ethylene proceeds much faster than the conversion from di-$\sigma$ ethylene to $\pi$ ethylene, there is a temporary massive accumulation of di-$\sigma$ ethylene. After all oxygen has been consumed, the coverage of di-$\sigma$ ethylene will decrease in favour of $\pi$ ethylene, which occupies only one site. This process increases the amount of ethylene adsorbed on the surface. At the end of the rich period, a dynamic equilibrium between the two ethylene surface species exists, with a small number of vacant sites.

When switching back to oxygen in the gas phase, at 10-11 s, oxygen adsors on the vacant sites, and rapidly oxidises the $\pi$ ethylene species. This creates many vacant sites, which facilitates the transformation of $\pi$ ethylene to di-$\sigma$ ethylene as expressed by the temporary increase of the di-$\sigma$ ethylene coverage. This transformation will stop and reverse when most of the $\pi$ ethylene species have disappeared, and finally part of the remaining di-$\sigma$ ethylene will be either combusted directly by oxygen or converted to $\pi$ ethylene and subsequently oxidised.
3.6. Simultaneous oxidation of carbon monoxide and ethylene

The model equations (3.6-3.12) and the acquired model parameters have been combined with the transient model for CO oxidation (Nibbelke et al., 1998a) in order to obtain a model for the kinetics of the combined ethylene and carbon monoxide oxidation. In this model, it is assumed that carbon monoxide, like ethylene, is able to adsorb and react on the carbonaceous layers. An adequate description of the combined ethylene and carbon monoxide oxidation experiments is obtained after adaptation, via regression, of the following three catalyst properties: 1) the noble metal capacity, 2) the fractional coverage of the deposited carbonaceous layer, 3) the oxygen storage capacity. None of the kinetic rate parameters were adapted, since these are unlikely to change when other components are present. In practice, the catalyst showed initially a very strong deactivation, occurring within the first hours of exposure to ethylene as mentioned before. During TPD experiments, ethylene was also found at temperatures above 500 K. This indicates that a part of the deposited species would still be ethylene or could recombine to ethylene. CO is known to be able to remove ethylene from noble metal surfaces through processes like cross desorption (Cider & Schöön, 1991). An indication for this can be seen in figure 3.2b, at $t = 8$ s, where the ethylene outlet concentration temporarily exceeds its inlet concentration. This item will be discussed in paragraph 3.6.1. The mentioned cross desorption could make the deactivation through deposition of carbonaceous species reversible. Therefore a lower fraction of deposited carbonaceous species and a higher noble metal capacity could be the result during CO plus ethylene oxidation, in comparison to ethylene-only-oxidation. The noble metal capacity was changed from 6.3 mmol/kg to 9.0 mmol/kg and the fractional coverage of carbonaceous deposits was changed from 0.66 to 0.6.

The value for the oxygen storage capacity, as was reported by Nibbelke et al. (1998a), had to be decreased from 6.0 mmol/kg to 2.2 mmol/kg, in order to obtain an adequate description of the experimental data. This could also be due to the spill over of carbonaceous species onto the ceria during the initial deactivation period, in line with the reported carbon deposition around noble metal particles (Bernal et al., 1999).
If it is assumed that carbon monoxide is unable to adsorb and react on the deposited carbonaceous species, an inadequate model prediction is found, especially for the CO\(_2\) signal, even if the three catalyst sorption capacities are adapted.

**3.6.1. Comparison of model predictions and experiments for CO/C\(_2\)H\(_4\) oxidation**

The predictions from the combined model are compared with the experimental data in figures 3.2b and 3.2c. The calculated water concentration at the end of the reactor is displayed as well in figure 3.2c. Although water could not be quantitatively measured, its model prediction provides insight with respect to CO\(_2\) produced by C\(_2\)H\(_4\) oxidation and by CO oxidation. The comparison of the combined model with the experimental data is adequate. Nevertheless, some deviations can be seen. First of all, the observed, small oxygen break through peak at \(t = 12\) s is not predicted by the model, while the opposite occurred for the ethylene-only-oxidation, see figure 3.1b. Whether or not an oxygen break through peak occurs is very sensitive for temperatures around 420 K (Nibbelke et al., 1998a). The desorption rate coefficients of ethylene and carbon monoxide are expected to have a large influence in this respect.

As in the ethylene-only-oxidation, the predicted CO\(_2\) peaks, in figure 3.2c, are somewhat retarded, which was ascribed to a slightly different sorption capacity of the support. The model is well able to predict the low CO\(_2\) peak, including its large shoulder, when switching from lean to rich at \(t = 7\) s. Immediately after switching, CO\(_2\) is produced from both C\(_2\)H\(_4\) and CO, as follows from the low water peak and the high CO\(_2\) peak. The second part of the "double CO\(_2\) peak" is solely caused by CO oxidation as the predicted water signal is zero. It is known that carbon monoxide adsorbs faster onto the noble metal and can also be oxidised faster than ethylene (Nibbelke et al., 1997a, Nibbelke et al., 1997b; Amon-Meziere et al., 1995, Sant & Wolf, 1989; Oh et al., 1986). Therefore CO combustion preferentially consumes the available adsorbed oxygen. Due to competitive adsorption with CO, the predicted ethylene outlet concentration (figure 3.2b) temporarily exceeds its inlet value (Cider & Schöön, 1991). The latter phenomenon is also reflected in the experimental data, figure 3.2b at \(t = 8\) s, but less pronounced.

The prediction of the break through of the CO signal is not exactly at the same time as was measured during the experiment, which could be related to some underestimation of ethylene desorption.

**3.6.2. Fractional surface coverages during CO and ethylene oxidation at the reactor outlet**

Figure 3.4 shows the model predictions of the fractional surface coverages on the noble metal and on the oxygen storage capacity at the end of the reactor. As expected, the highest fractional coverage during the rich period is the CO coverage (\(t = 11\) s). When the switch to the oxygen feed is made (\(t = 12\) s), both carbon monoxide and \(\pi\) ethylene coverages decrease very rapidly. The increase in vacant sites, through combustion reactions, leads to an increase in the coverage of the refractory di-\(\sigma\) ethylene. After all \(\pi\) ethylene has been converted, the remaining di-\(\sigma\) ethylene is slowly oxidised. The coverage of oxygen on the noble metal increases faster than the oxygen coverage on ceria (OSC), despite the fact that ceria sites are vacant at the moment of switching. The large difference in rate constants for adsorption on the noble metal and on the OSC (Nibbelke et al., 1998a; Nibbelke et al., 1997a) is an indication in this respect. The maximum value of the oxygen surface coverage is about 0.6.
When at about 7 s a switch from lean to rich is made, the conversion of carbon monoxide at the reactor outlet is still 100% for approximately 1 s. Hence, the surface coverage of CO will be low, which enables considerable ethylene adsorption in the di-σ mode. Any π ethylene, formed from di-σ ethylene, will be immediately combusted as long as there is oxygen left on the noble metal. As soon as the oxygen coverage on the noble metal reaches zero, π ethylene oxidation decreases as indicated by the gradual rise in its coverage. The di-σ ethylene coverage passes a maximum due to transformation into π ethylene and desorption of ethylene (Cider & Schöön, 1991). This latter effect led to the temporary rise of the ethylene outlet signal above the inlet signal. In between 8.0 and 8.3 s, there is no oxygen consumption at the reactor outlet, as indicated by the constant coverage of oxygen on ceria and the zero oxygen coverage on the noble metal. The CO conversion, however, is still complete. Apparently, during this interval all CO is adsorbed and converted by oxygen into CO₂ in the upstream part of the reactor. As the oxygen on ceria is only available for CO, it will be consumed after all noble metal oxygen is converted. This indicates that after the lean to rich switch the oxidation of CO mainly takes place in the first part of the reactor, while the ethylene conversion only occurs at the end of the reactor as long as CO did not yet reach the outlet. Indeed, it was observed during experiments with higher CO partial pressures that hardly any ethylene was converted. As soon as the ceria oxygen source has depleted, the CO coverage starts to rise at the expense of di-σ ethylene, which is either slowly oxidised or transformed into fewer sites occupying π ethylene. At the end of the rich half cycle, the surface is mainly covered with C₂H₄* and CO* until the switch to the lean feed is made again.

3.6.3. Model predicted reactor profiles during CO and ethylene oxidation

In order to get more insight into the combined CO and C₂H₄ oxidation, typical model predicted reactor profiles of the gas phase concentrations and fractional surface coverages have been plotted in figures 3.5 and 3.6, at time t = 7.7 s, as indicated in figure 3.2 by the vertical dotted line. The switch from lean to rich has been made shortly before, around 7.0 s. Ethylene is breaking through, the CO₂ concentration has just passed its maximum and CO is still being fully converted. Figure 3.5 shows the gas phase concentrations versus the co-ordinate of the catalyst bed. The end of the reactor is located at x = 15 mm. The oxygen concentration is zero everywhere in the reactor. It can be seen that the CO concentration reaches zero within the first 7 mm of the reactor. The CO concentration curve and the CO₂
concentration curve cross each other at their inflection points, near \( x = 6 \) mm, indicating that the CO oxidation rate is highest. Up to this point in the reactor the water concentration is almost zero, meaning that ethylene is not converted in the front part of the reactor. The ethylene concentration even rises along the reactor axis up to the point where the CO concentration reaches zero, due to competitive adsorption. As long as CO is available in the gas phase, it will immediately occupy vacant sites, created by ethylene desorption. It induces an extra ethylene transport in the downstream direction, and the local ethylene concentration may exceed the inlet concentration.

![Figure 3.5. Model predicted gas phase concentrations versus the reactor axis, at \( t = 7.7 \) s during the experiment, displayed in figure 3.2.](image)

When CO is completely removed from the gas phase, ethylene can adsorb and react, as expressed by the rising water concentration from \( x = 6 \) mm onwards. The maximum in the ethylene concentration, near \( x = 6 \) mm, will reach the reactor outlet around \( t = 9 \) s as can be seen in figure 3.2b.

The corresponding fractional surface coverages versus the reactor co-ordinate are depicted in figure 3.6. The noble metal coverage with oxygen adatoms is nearly zero in the front part of the reactor, in line with the general insight that the availability of oxygen limits the CO oxidation rate (Nibbelke et al., 1997a; Jen et al., 1999). The fractional coverages of CO* and OCO* follow the gas phase concentration of CO. The OCO* coverage is the first to approach to zero. Gas phase CO still inhibits the ethylene oxidation, as CO adsorbs very fast on the noble metal and reacts with oxygen from ceria via the bifunctional reaction path (Nibbelke et al., 1997a). Around \( x = 6 \) mm, this contribution is considerable, as reflected by the large increase of the CO2 gas phase concentration (figure 3.5) and by the drastic change in the oxidation storage capacity (figure 3.6). It is well known that oxygen from ceria is very rapidly converted by CO as soon as all noble metal oxygen has been depleted (Nibbelke et al., 1998a; Nibbelke et al., 1997a). This oxygen from ceria is not involved in ethylene oxidation. The vacant sites in the first part of the reactor, created by CO oxidation, are filled primarily by di-\( \sigma \) ethylene, which is not converted because of its low reactivity compared to CO. A minor fraction is transformed into \( \pi \) ethylene. In the second part of the reactor, \( x > 6 \) mm, the coverages of both ethylene surface species decrease gradually due to combustion.
Near the end of the reactor, the remainder of sites is still covered with oxygen adatoms from the previous half-cycle.

![Fractional surface coverages](image)

The results from figures 3.4 and 3.6 show that cycling of the feed induces spatio-temporal patterns in the reactor. CO is always oxidised in the front part of the reactor, and ethylene in a subsequent zone. As such, the results agree with simulation studies by Nievergeld et al. (1997a,b), who composed a kinetic scheme for reactions in an automotive exhaust gas, using a mixture of elementary steps from various literature sources. They showed that in a monolithic converter automotive exhaust gas components react sequentially in rather distinct zones. Just after switching from lean to rich, the CO oxidation zone is very narrow, because of a high surface coverage with oxygen adatoms, which makes the Eley-Rideal path via the OCO* species the major contributor. The rest of the reactor is available for oxidation of ethylene, which is also fully converted. With increasing time, surface oxygen depletion at the reactor inlet causes expansion of the CO oxidation zone, which pushes the zone for C2H4 oxidation towards the end of the reactor. It leads gradually to a decreasing ethylene conversion, and finally to lower CO conversion. The sharp front, where depletion of the oxygen storage capacity occurs, also travels through the reactor from inlet to outlet. Similar reasoning can be applied for the lean half cycle.

The periodical high level of outlet C2H4 concentrations, which exceeds the inlet concentration, is a typical equivalent of what is known as wrong-way-behaviour of automotive converters (Oh & Cavendish, 1982; Zygourakis, 1989). If the inlet temperature would be decreased stepwise, a heat front moves through the reactor, causing a temporary increase of the outlet reactor temperature.

### 3.7 LEIS measurements

#### 3.7.1. Introduction

In this section Low-Energy Ion Scattering (LEIS) has been used to quantify the coke formation on the commercial three-way catalyst, used to determine the kinetics of ethylene
oxidation. Using LEIS the elemental composition of the outermost atomic layer of a catalyst can be determined in a quantitative way. Hence, if the catalyst surface is partly covered with carbon this will both be detected by observing the presence of carbon and by measuring the disappearance of the underlying material. Therefore, LEIS can reveal whether the carbon is deposited on the carrier material or on the noble metals. The high sensitivity of LEIS towards noble metals enables detection down to concentrations of some 10 ppm of a monolayer. The noble metal surface areas of fresh and used catalysts as detected with LEIS, have been compared with the corresponding values determined by kinetic modelling of the acetylene (Chapter 4) and ethylene+carbon monoxide oxidation at cold start conditions, to verify the outcome of the latter.

3.7.2. Experimental

In LEIS (also known as Ion Scattering Spectroscopy or ISS) experiments, low-energy noble gas ions are scattered by atoms in the exposed surface. According to the laws of conservation of energy and momentum, the energy spectrum of the back-scattered ions is equivalent to the mass spectrum of the target atoms. The information depth of LEIS is limited to one atomic layer, because of the high neutralisation probability of the noble gas ions.

Prior to LEIS analysis the catalyst samples have been compacted into pellets at 300 MPa. Recently, it has been proven that compaction at 300 MPa does not influence LEIS analysis (Jansen et al., in press). LEIS selectively probes the outermost atomic layer, hence surface contaminants would obscure the intrinsic composition. Therefore, the contaminants have to be removed before analysis of the intrinsic composition is possible. To clean the fresh, and to regenerate the used three-way catalyst samples, an atomic oxygen beam has been applied. The use of atomic oxygen allows very effective cleaning at low temperatures (ca. 310 K). After the oxidative cleaning, the catalysts are reduced at 573 K in 20 kPa H₂ flowing at 2.6 mmol/min for 10 minutes.

After evacuation, hydrogen from the reduction treatment remains on the catalyst surface. This remaining hydrogen can be selectively removed by sputtering, since the sputter rate for hydrogen is usually 10 to 50 times higher than that for other elements (Bergman, 1996). From LEIS measurements as a function of ion dose, it appeared that hydrogen was removed upon a He dose of 2×10¹⁵ ions/cm². Between a He dose of 2×10¹⁵ ions/cm² and 10×10¹⁵ ions/cm², the surface composition of the catalyst remained constant. The sputter rate of Ne is typically 10 times higher than for He. Therefore, all presented measurements are carried out using either a He dose between 2×10¹⁵ ions/cm² and 9×10¹⁵ ions/cm² or a Ne dose between 0.2×10¹⁵ ions/cm² and 1×10¹⁵ ions/cm².

All LEIS measurements have been performed in the UHV Calipso LEIS set-up. This set-up, which has been developed at the Eindhoven University of Technology, is equipped with a sensitive double-toroidal analyser and a large position-sensitive detector. These allow to measure a large part of the energy spectrum simultaneously (Ackermans et al., 1988).

To analyse the surface composition of the three-way catalyst before and after use in the ethylene and acetylene oxidation, 3 keV ⁴He ions have been used. Moreover, 3 keV Ne ions have been used to allow separation of Pt from the Ce in the catalyst carrier. Unfortunately, Rh cannot be observed since the expected Rh surface concentration is ca. 10 times lower than the Pt surface concentration because of segregation (Jansen et al., submitted). Moreover, the Rh peak is on the low-energy side of the huge Ce peak. Hence a small Rh peak is indiscernible
from the Ce background of the catalyst carrier. The beam was rastered over an area of $1 \times 1$ mm$^2$ during measurements. In the Calipso LEIS set-up the primary ion beam is directed perpendicular towards the target, and ions scattered over 145° with respect to the incoming beam are detected. During the experiments the catalyst samples were prevented from charging by flooding with low-energy electrons from all directions.

3.7.3. Results

3.7.3.1. LEIS analysis of the catalyst carrier

Figure 3.7 shows LEIS spectra of a fresh (solid line) and a used (dotted line) Pt/Rh/CeO$_2$/\(\gamma\)-Al$_2$O$_3$ three-way catalyst.

The spectra have been measured with a 3 keV $^4$He dose of $6 \times 10^{15}$ ions/cm$^2$, and are therefore selectively representing the outermost atomic layer of the catalyst. From this figure, it can be seen that the catalyst surface exposes not only large amounts of Ce, O, and Al, but also a significant amount of F. Additional measurements on the support materials revealed that the F originates from the \(\gamma\)-Al$_2$O$_3$ support material. Like other surface contaminants, F will obscure underlying catalyst constituents. Since the F content differs from sample to sample, it hampers exact quantification of the composition of the catalyst support. However, the Al peak area is about twice as high as the Ce peak area. In combination with the fact that Ce is much heavier and therefore more easily detected than Al, this shows that there is much more Al in the surface than Ce. This is in agreement with the bulk analysis of the diluted three-way catalyst being 11 weight % CeO$_2$ and 89 weight % \(\gamma\)-Al$_2$O$_3$ (Campman, 1996).

3.7.3.2. LEIS analysis of the Pt surface area after acetylene oxidation

To allow separate determination of Pt and Ce, 3 keV Ne ions have been used. Figure 3.8 shows the Pt LEIS signals for a fresh three-way catalyst (dotted line), the catalyst after use in the acetylene oxidation (thick solid line), and the catalyst after regeneration following use in the acetylene oxidation (thin solid line). Prior to the LEIS measurements, the fresh catalyst has been cleaned using atomic oxygen, whereupon it was reduced at 573 K. As has been described in the previous section, these treatments have been carried out to reveal the intrinsic catalyst surface. To regenerate the catalyst after use in the acetylene oxidation, the same treatment has been applied. The figure shows the Pt signal decreased 50%±5% after use in the acetylene oxidation at cold start conditions. This decrease in Pt signal can be explained in two ways, either half of the Pt is covered by some other material, or severe sintering took place during use. An eightfold volume increase of the Pt particles due to sintering is needed to explain a 50% signal decrease. This is highly improbable during use at 543 K, especially since both the fresh and the used catalyst have been exposed to 773 K during the pre-treatment. As shown in figure 3.8, the Pt surface concentration could be completely restored after regeneration.

LEIS data are generally independent of the chemical environment (i.e. no matrix effects) (Brongersma et al., 1994; Taglauer, 1991). Therefore, the sensitivity for Pt can be calibrated against a reference sample with a well-known Pt surface atomic density. The Pt surface concentration of the three-way catalyst has been calibrated against a sputter cleaned pure polycrystalline Pt sample. From this, it was learned that the Pt surface concentration in the fresh three-way catalyst equals approximately 0.040% of a monolayer. However, this concentration is obtained on a three-way catalyst that has been diluted with inert $\alpha$-Al$_2$O$_3$. If correction for the dilution is applied, a Pt surface concentration of 0.098% of a monolayer for the pure fresh three-way catalyst is found. If 50% of this amount is covered with
carbonaceous species, this cannot be detected in the carbon LEIS signal, since the sensitivity for carbon is too low. However, the high sensitivity for Pt allows detection of the Pt surface concentration loss.

The Pt surface concentration can be entirely restored during regeneration, or cleaning. This proves that no sintering took place during use. The loss in Pt signal is due to a 50%±5% coverage of the Pt with carbonaceous species, deposited during acetylene oxidation. These carbonaceous species can be effectively removed using atomic oxygen and a consecutive reduction at 573 K.

3.7.3.3. Comparison between LEIS analysis and kinetic modelling

LEIS analysis reveals that three-way catalysts that have been used in ethylene oxidation at cold start conditions show a 51%±5% decrease in Pt surface concentration as well. Table 1
summarises the relative Pt surface concentrations found with LEIS and compares them to those obtained with kinetic modelling by from this chapter and chapter 4. The experimental error margin for LEIS analysis is mainly caused by the determination of the Pt peak area. Since both peak area determinations have an accuracy of 7%, a 10% error margin is estimated for the peak area ratio of the fresh and the used catalyst.

For the data obtained by kinetic modelling, the error estimation is more difficult, because the statistical data from transient regression analysis is unreliable, due to the fact that successive measurements in time are not independent. The kinetic modelling results revealed a 60% and a 40% reduction of the Pt surface concentration in case of acetylene and ethylene + carbon monoxide (section 3.6), respectively. This is of the order of magnitude of the 50% reduction found in the LEIS experiments. This value of 50% Pt surface reduction has been used in model simulations of the ethylene + carbon monoxide and acetylene conversion. It was found that this value of 50% could also well describe the experimental data. At higher and lower values than 0.6±0.1, no accurate description of notably the carbon dioxide concentrations can be obtained. This indicates an uncertainty of approximately 0.1 for the kinetic modelling results in the normalised Pt surface concentration. This error margin is given in table 3.4.

Consequently, the observed 50±5% or 51±5% decrease in Pt surface concentration after use in respectively acetylene or ethylene oxidation, as found with LEIS, agrees quantitatively with the noble metal area loss found in kinetic modelling.

| Table 3.4. The Pt surface concentration normalised to a fresh three-way catalyst. |
|---------------------------------|-----------------|-----------------|
| Fresh three-way catalyst        | LEIS            | Kinetic Modelling |
| Three-way catalyst used in      | 0.50±0.05       | 0.4±0.1          |
| acetylene conversion            |                 |                  |
| Three-way catalyst used in      | 0.49±0.05       | 0.6±0.1          |
| ethylene conversion             |                 |                  |
| Regenerated three-way catalyst  | 1.1±0.1         | -                |

3.8. Conclusions

The transient oxidation of ethylene by oxygen was studied via cycling of the feed over a Pt/Rh/CeO$_2$/$\gamma$-Al$_2$O$_3$ catalyst. Experiments, under conditions representing the cold start of an Otto motor, indicate the presence of two types of adsorbed species, which are ascribed to $\pi$- and di-$\sigma$ ethylene. The former species can be oxidised rapidly, while the latter one is rather refractory. No intermediate products were detected. The presence of ceria does not influence the ethylene oxidation at the investigated conditions.

A kinetic model, based on elementary steps has been proposed, which is able to predict adequately the experimental data for both rich and lean half cycles with one set of rate parameters. An assumption was made about deposition of carbonaceous species, leading to selective deactivation. Experimental indications for this phenomenon have been found.

Extension of the proposed model with a published transient model for CO oxidation (Nibbelke et al., 1998a) on the same catalyst adequately describes the experimental data of combined ethylene and carbon monoxide oxidation. Carbon monoxide inhibits the conversion of ethylene and is oxidised in the front part of the reactor. The region for ethylene
combustion is located at the end of the reactor. Cycling of the feed induces spatio temporal patterns in the reactor.

LEIS analysis shows a Pt surface concentration of about 0.098% of a monolayer in a fresh commercial three-way catalyst. After use in either acetylene or ethylene oxidation at cold start conditions, a decrease of 50±5% of the Pt surface concentration is observed with LEIS. The Pt surface concentration can be completely restored by exposing the used catalyst to atomic oxygen and a subsequent reduction at 573 K. Therefore, the observed Pt loss is not due to sintering, but due to deposition of carbonaceous species during the hydrocarbon oxidation. The observed loss in Pt surface area with LEIS agrees quantitatively with the noble metal area loss as found in kinetic modelling of acetylene and ethylene oxidation, being 60±10% and 40±10%, respectively. Hence, this study shows that LEIS can be successfully applied to quantitatively investigate coke formation on commercial supported three-way catalysts.

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KINETICS OF ACETYLENE OXIDATION OVER Pt/Rh/CeO2/γ-Al2O3

The part on the steady state kinetics of acetylene oxidation will be published in Topics in Catalysis, the part on transient kinetics has been published in Chem. Eng. Sci. 56(6), 2001, 2019

Abstract
The steady state and transient kinetics of acetylene (C2H2) conversion by oxygen over a commercial Pt/Rh/CeO2/γ-Al2O3 three-way catalyst have been modelled. Experiments to determine rate parameters for the models were carried out in a fixed-bed reactor. The experimental conditions resemble the cold-start period of an Otto engine. Steady state experiments show that acetylene inhibits both adsorption of itself and of oxygen. Acetylene is first converted to CO on the catalytic surface. For the transient experiments, alternate feeding of acetylene and oxygen has been applied at frequencies of feed composition cycling up to 1/6 Hz. Two types of adsorbed acetylene species seem to exist. A selective catalyst deactivation for oxygen adsorption, due to deposition of carbonaceous deposits, was found. Ceria proved to have a significant influence on the acetylene oxidation. Kinetic models were developed for the steady state and transient conversion of acetylene to carbon monoxide, based on elementary reaction steps. The transient model consists of the same reaction steps as the steady state model plus additional steps, required to explain phenomena not observed under steady state conditions. These models were both combined with the published kinetics for transient carbon monoxide oxidation to carbon dioxide over the same catalyst (Nibbelke et al., 1998a), in order to describe the total oxidation of acetylene quantitatively. The steady state model gives a reasonable prediction of the measurements. The combined transient model is able to describe the results of the transient experiments on simultaneous acetylene and carbon monoxide oxidation. During a transient, both acetylene and carbon monoxide react mainly in a front moving through the reactor, carbon monoxide hardly influencing the acetylene oxidation.

4.1. Introduction

In this chapter, the oxidation of acetylene is studied because acetylene has a strong inhibitive effect on catalyst light off during the cold start. For noble metal catalysts, all acetylene should be converted before other hydrocarbons and carbon monoxide can react (Bart et al., 1992; Mabilon et al., 1995; Amon-Meziere et al., 1995). According to Impens (1987), 20 mol % of the total hydrocarbons in an exhaust gas is acetylene, which makes it one of the most abundant hydrocarbons next to ethylene (25 mol %), and methane (20 mol %). Immediately after the start of an engine, the percentage of acetylene emitted by the engine becomes as high as 17 wt. %, which would mean at least 25 mol %. During progression of the cold-start
period the percentage decreases to 10 wt % after 34 s, while still 4 wt. % acetylene is present in the exhaust gas after 150 s (Kubo et al., 1993). The latter value is obtained after catalyst light-off, and is confirmed by Drake et al. (1996), who report 5 % acetylene emission by the engine after light-off. Little is known from the literature about the kinetics of acetylene oxidation. Most studies are qualitative and have been performed under UHV conditions. Kinetic modelling studies have not been reported. Acetylene very strongly adsorbs onto noble metal surfaces, due to its large electron donor effect (Amon-Meziere et al., 1995). A sticking coefficient near unity was reported on several occasions (Mabilon et al., 1995; Dannetun et al. 1986; Palmer, 1977). Also, acetylene is able to adsorb immediately on an oxygen-covered surface (Dannetun et al. 1986; Palmer, 1975). Megiris et al. (1985) found both decomposition and oxidation products, when adsorbing acetylene on an oxygen-covered noble metal surface. They conclude that oxidation takes place at the interface of acetylene and oxygen islands on the surface. According to Cider and Schöön (1991) and Mabilon et al. (1995), acetylene is able to remove adsorbed species, like ethylene and carbon monoxide, from the surface through cross desorption under transient conditions.

The electron donor effect makes acetylene refractory towards oxidation (Amon-Meziere, 1995). Therefore, acetylene does not only inhibit its own oxidation, but also the oxidation of other hydrocarbons and carbon monoxide. The light-off temperature of the latter species is increased by 100 K if acetylene is present in the reactor feed gas (Amon-Meziere, 1995). Mabilon et al. (1995) observed that the light-off temperature of both carbon monoxide and nitric oxide increased with increasing acetylene concentration. Only methane oxidation is not influenced by the presence of acetylene, due to the very high light-off temperature of methane.

Many types of adsorbed acetylene species are reported in the literature. A π-bonded acetylene, on a single active site, has been found by Kesmodel et al. (1977). This type of adsorbed acetylene species is said to be metastable. A double bonded di-σ acetylene has been reported by Reid et al. (1973) and Megiris et al. (1985), but its presence is questioned by Kesmodel et al. (1977). The triple bonded acetylene is the most reported surface form of acetylene (Kesmodel et al., 1977; Reid et al., 1973; Cremer et al., 1977; Ibach and Lewald, 1978; Kang and Anderson, 1985; Mate et al., 1988). This type of species is found to be the most stable type of adsorbed acetylene. Finally, an acetylene species bonded to four sites is only reported by Reid et al. (1973).

At low surface coverages of acetylene (adsorbed on an empty surface), acetylene will decompose to species like vinylidene (=C=CH\textsubscript{2}) and ethylidyne (≡C-CH\textsubscript{3}) (Megiris et al., 1985; Cremer et al., 1997; Berlowitz et al., 1985). During this decomposition, hydrogen will desorb (Palmer, 1975; Megiris, 1985). Eventually, only carbon will remain on the surface (Dannetun et al., 1986; Palmer, 1975; Reid et al., 1973; Kang and Anderson, 1985). If carbon monoxide is pre-adsorbed on the surface, the decomposition is prevented (Reid et al., 1973), indicating that vacant sites are required for acetylene decomposition. If acetylene is adsorbed on a hydrogen covered surface, ethylene and ethane are produced also (Megiris et al., 1985; Reid et al., 1973).

Acetylene adsorption on an oxygen-covered surface leads to both carbon monoxide and carbon dioxide formation (Palmer, 1975; Megiris et al., 1985; Berlowitz et al., 1985) as well as H\textsubscript{2}O production. However, Dannetun et al. (1986) did not observe any carbon monoxide. During Temperature Programmed Oxidation experiments (Megiris et al., 1985), water was detected before the appearance of carbon monoxide and carbon dioxide. This could indicate
that acetylene first is partially oxidised to water and carbon monoxide, which is sequentially oxidised to carbon dioxide.

This chapter reports the results of experimental work and kinetic modelling for the steady state and transient acetylene oxidation by oxygen under Otto engine cold start conditions. Furthermore, the transient simultaneous acetylene and carbon monoxide oxidation is studied. Results are quantitatively described by combining the currently presented models with a previously published model for the transient carbon monoxide oxidation on the same catalyst (Nibbelke et al., 1998a). The modelling work in this paper does not distinguish between Pt and Rh surface sites. Mate et al. (1988) report that acetylene bonding is the same on Pt(111), Rh(111) and Pd(111), and that surface behaviour of acetylene is similar as indicated by Reid et al. for Rh/SiO₂.

The fact that acetylene must be oxidised, before other hydrocarbons and CO can be oxidised or NO can be reduced, has been reported for Pt/Rh (Bart et al., 1992, Mabilon et al., 1995) and for Pd/Rh three-way catalysts (Amon-Meziere et al., 1995). The reactivity of various individual hydrocarbons has been expressed as light-off temperature for both Pt/Rh and Pd/Rh catalysts by the same authors. For both catalysts the order of decreasing reactivity is the same: alkenes ≈ alcohols ≥ alkynes >> alkanes. For most hydrocarbons they found a lower light-off temperature on Pt/Rh than on Pd/Rh three-way catalysts, but for acetylene and methane a reversed effect was observed. So, the qualitative behaviour of the noble metals seems the same, but the type of adsorbate is important.

4.2. Experimental

The experimental set-up, used for the transient oxidation of acetylene and carbon monoxide via cyclic feeding, and the catalyst treatment procedures have been described in chapter 2. During the steady state experiments, only one feed line was used. Both steady state and transient analysis was performed by an on-line quadrupole mass spectrometer (VG Sensorlab 200D). Mass spectrometry analysis was carried out with a frequency of 120/n Hz, with n the number of masses analysed. Analysis was performed on masses 4 (He), 26 (C₂H₂), 28 (CO+CO₂), 32 (O₂), and 44 (CO₂). Water was not measured.

Reproducible experimental data were obtained by avoiding slow deactivation due to oxidation of the noble metal particles (Carbello and Wolf, 1978; Burch and Hayes, 1995; Hiam et al., 1968) through alternating a rich feed and a lean feed over the catalyst continuously. The range of the experimental conditions is depicted in table 4.1.

<table>
<thead>
<tr>
<th>Table 4.1. Range of experimental conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature K</td>
</tr>
<tr>
<td>total pressure kPa</td>
</tr>
<tr>
<td>p₀ C₂H₂ kPa</td>
</tr>
<tr>
<td>p₀ O₂ kPa</td>
</tr>
<tr>
<td>p₀ CO kPa</td>
</tr>
<tr>
<td>W/F (steady state) gcat mol⁻¹</td>
</tr>
<tr>
<td>W_cat 10⁻³ kg_cat</td>
</tr>
<tr>
<td>cat dilution m₃ inert m⁻³ m₃ inert+cat</td>
</tr>
<tr>
<td>transient conditions:</td>
</tr>
<tr>
<td>frequency Hz</td>
</tr>
<tr>
<td>duty cycle %</td>
</tr>
</tbody>
</table>
4.3. Steady state kinetics of acetylene oxidation

4.3.1. Modelling

The fixed-bed reactor, used in this study, is regarded as an ideal isothermal plug flow reactor in the steady state, with a constant total molar flow rate along the catalyst bed. The reactor model consists of the continuity equations for
1) C₂H₂, O₂, CO, and CO₂ in the gas phase,
2) surface species adsorbed on the noble metal surface,
3) oxygen adsorbed on ceria (OSC).

The continuity equation for gas phase component i is as follows:

\[
\frac{1}{\tau} \frac{\partial C_i}{\partial z} = \frac{\rho_B}{\varepsilon_B} \sum_k L_k R_{k,i}
\]

(4.1)

with boundary condition: \( z = 0, \ C_i = C_i^{IN} \). The symbols are explained in the section “Nomenclature”.

The continuity equations for species j adsorbed on the noble metal surface (\( k = NM \)), and species m on ceria (\( k = OSC \)) can be written as follows:

\[
\sum_k L_{NM} R_{k,j} = 0 \quad (4.2)
\]

\[
\sum_k L_{OSC} R_{k,m} = 0 \quad (4.3)
\]

For \( L_{NM} \) a value of 0.012 mol kg\(^{-1}\) was taken as determined by CO chemisorption. The value of 0.006 mol kg\(^{-1}\) for \( L_{OSC} \) was taken from (Nibbelke et al., 1998a), and refers to oxygen on the ceria surface only.

The production rates in Equations (4.1), (4.2), and (4.3) can be calculated from the rates of the elementary reaction steps in the reaction mechanism:

\[
\sum_{p=1}^{M} v_{i,p} r_{w,p} = 0 \quad (4.4)
\]

The reaction rates \( r_{w,p} \) of the elementary reaction steps were calculated via the law of mass action, while restricting the adsorption capacity to a monolayer as maximum.

A backward differentiation formula integrator from the NAG Fortran library (NAG, 1997), routine D02NHF, was used for calculating the steady state solution of Equations (4.1), (4.2), and (4.3). The numerical calculations were carried out on a Silicon Graphics CRAY Origin2000. The typical CPU time for simulating a set of experiments amounts to approximately 10 s.

The conversion of acetylene was calculated by:

\[
X_{C_2H_2} = \frac{F_{C_2H_2}^{IN} - F_{C_2H_2}^{OUT}}{F_{C_2H_2}^{IN}} \cdot 100\%
\]

(4.5)

The selectivity towards CO was defined as:

\[
S_{CO} = \frac{F_{CO}^{OUT}}{F_{CO}^{OUT} + F_{CO_2}^{OUT}} \cdot 100\%
\]

(4.6)
Estimation of the kinetic parameters was performed with non-linear multi-response regression analysis, applied to the conversion of acetylene and the selectivity towards CO. The following objective function was minimised:

\[
S(b) = \sum_{q=1}^{v} \sum_{i=1}^{n} w_{i,q} [y_{i,q} - g_{q}(x_{i}, b)]^2 \rightarrow \text{minimum}
\]  

(4.7)

The symbols are explained in the section ‘Nomenclature’ of this thesis. The function represents the weighted sum of squares for all measured gas phase concentrations all experiments. Minimisation was achieved with a multi-response Levenberg-Marquart algorithm (Froment & Hosten, 1981; Boggs et al., 1992). The regression of the steady state acetylene oxidation experimental data was carried out for a total set of 105 separate experiments at temperatures of 503, 523, and 543 K. All weight factors were set to \(1/y_{i,q}\). In order to avoid strong correlation between the Arrhenius parameters, the Arrhenius equations were reparametrised according to Kitrell (1970).

### 4.3.2. Experimental results

In figure 4.1, the acetylene conversion and the selectivity to carbon monoxide have been plotted versus the reactor space time, represented as the W/F\(^0\) ratio (i.e. the total mass of the catalyst, divided by the total gas flow rate), at a temperature of 523 K, an oxygen inlet partial pressure of 0.55 kPa, and an acetylene inlet partial pressure of 0.15 kPa. The conversion of acetylene rises linearly with increasing reactor space time, indicating differential reactor operation with respect to the acetylene consumption. With decreasing space time, the selectivity to CO approaches towards 100%. This indicates that CO is the only primary reaction product in the oxidation of acetylene: acetylene is first converted to CO, which can then either desorb into the gas phase, or be oxidised to CO\(_2\), which is the sequential product. If the selectivity to CO would reach a lower value than 100% at zero space time, two parallel reaction paths would exist: one directly to CO\(_2\), and the other via CO to CO\(_2\). Apparently only the latter path is important.

![Figure 4.1.](image_url)
Figure 4.2A shows the dependence of the conversion of acetylene on the inlet oxygen partial pressure at three temperatures and an acetylene inlet partial pressure of 0.1 kPa. As can be seen, the conversion increases with increasing oxygen partial pressure and temperature. This means that the partial reaction order of oxygen is positive, in line with published results (Amon-Meziere et al., 1995; Bart et al., 1992). Figure 4.2B shows that the selectivity to CO decreases with increasing oxygen partial pressure. This is also expected, because the presence of additional oxygen will favour the sequential reaction of CO to CO₂. It is also noticeable that the selectivity to CO decreases with increasing temperature. This could mean that the sequential oxidation of adsorbed CO is more activated than CO desorption, which is, however, not in line with published data (Nibbelke et al., 1998a). Increasing the temperature leads to a higher oxidation rate of acetylene, which will yield vacant sites. These vacant sites will become relatively more occupied with oxygen than acetylene, as the C₂H₂ coverage is already very large. A higher fractional coverage of oxygen stimulates the direct adsorption of CO onto oxygen adatoms (Nibbelke et al., 1998a), which will eventually produce gaseous CO₂, i.e. a lower selectivity.

Figure 4.2. The conversion of acetylene (A) and the selectivity to CO (B) versus the inlet oxygen partial pressure at temperatures of 503, 523, and 543 K, and an acetylene inlet partial pressure of 0.10 kPa. Markers indicate experimental results, curves are model predictions. ◆ measurements at T = 503 K, ▲ measurements at T = 523 K, ■ measurements at T = 543 K, - - - model predictions at T = 503 K, — model predictions at 523 K, ⋯ model predictions at 543 K.

Figure 4.3. The conversion of acetylene (A) and the selectivity to CO (B) versus the inlet acetylene partial pressure at temperatures of 503, 523, and 543 K, and an oxygen inlet partial pressure of 0.55 kPa. Markers indicate experimental results, curves are model predictions. ▲ measurements at T = 503 K, ◆ measurements at T = 523 K, ■ measurements at T = 543 K, - - - model predictions at T = 503 K, — model predictions at 523 K, ⋯ model predictions at 543 K.
Figure 4.3A shows that the conversion of acetylene decreases with increasing acetylene inlet partial pressure. It means that the partial reaction order of acetylene is negative, due to self-inhibition by acetylene, which is more pronounced at higher temperatures. The corresponding influence of the acetylene inlet partial pressure on the selectivity to CO can be seen in figure 4.3B. The higher the acetylene inlet partial pressure, the more CO is produced. This again is due to inhibition by acetylene, which makes the catalyst surface not accessible for oxygen. The selectivity to CO is highest at the lowest investigated temperature.

4.3.3. Modelling results and discussion

Since carbon monoxide is the only primary reaction product, modelling of the oxidation kinetics of acetylene should be possible by combining the (elementary) reaction steps of the conversion of acetylene into carbon monoxide with those of the oxidation of carbon monoxide into carbon dioxide. For the latter, a transient kinetic model, settled for the same catalyst (Nibbelke et al., 1998a), was applied. Features of this model are: reversible adsorption of carbon monoxide; molecular oxygen adsorption, followed by instantaneous dissociation; CO₂ formation via a Langmuir-Hinselwood path, via a bifunctional path involving ceria, and via adsorption of CO on sites covered with O adatoms, so-called OCO species. This CO oxidation model was applied as such, without changing any of the reported rate parameters (Nibbelke et al., 1998a). Three steps were added, in order to describe the conversion of gaseous acetylene into adsorbed carbon monoxide. For one of these steps, the rate parameters could be taken from the literature. The parameters of the two remaining steps were estimated from regression of the data with the complete acetylene oxidation model. The following three steps were added:

1. **Irreversible adsorption of acetylene** (table 4.2, step 1). It was found that the adsorption of acetylene had to be first order in vacant sites; using higher orders did not yield satisfactory model predictions. It has been tried to model the adsorption of acetylene with involvement of more than one active site, but still with a first order in vacant sites on the catalyst surface. These models gave the same results as the model, in which acetylene occupies only one vacant site. During surface science studies, acetylene adsorbed on one single site was observed by Kesmodel et al. (1977). In the literature, sticking coefficients near unity have been reported (Mabilon et al., 1995; Dannetun et al., 1986; Palmer, 1977). This value was used here to calculate the adsorption rate coefficient, and was not adapted during regression. Although some acetylene is likely to desorb (Megiris et al., 1985), it will only be a very small amount at the conditions currently applied. Therefore in this study, the desorption constant has been set to an arbitrary low value of 10⁻¹⁰ s⁻¹, in order to avoid a transcritical bifurcation point (Nibbelke et al., 1998b).

2. **Conversion of adsorbed acetylene to adsorbed carbon monoxide and gaseous water via a Langmuir-Hinselwood surface reaction** (table 4.2, step 2). The reaction involves three oxygen adatoms, and is not an elementary reaction step. It is believed that the oxygen assisted abstraction of the most weakly bonded hydrogen atom (Amon-Meziere et al., 1995; Chapter 3) is the rate determining step, whereupon subsequent reaction steps towards adsorbed carbon monoxide can be considered as instantaneous. Models without oxygen assisted hydrogen abstraction were not able to predict the relation between the selectivity to CO and the reactor space-time. A similar situation was met in the partial oxidation of methane (de Smet et al., 2000), where modelling of oxygen assisted hydrogen abstraction was also required for an adequate description of the selectivity of CO versus the reactor residence time. Water desorption was taken instantaneous (Heras & Viscido, 1988).
3. Conversion of adsorbed acetylene into adsorbed carbon monoxide via a bifunctional path (table 4.2, steps 3a and 3b). In section 4.4, it has been found that the presence of ceria had a large influence on the oxidation of acetylene. This can be understood if one considers that the noble metal will almost completely be covered by acetylene, leaving very few vacant sites for oxygen adsorption. Ceria, however, will be still available for oxygen adsorption. At the interface between ceria and the noble metal particles, a bifunctional reaction may take place. This is also known to happen for CO (Nibbelke et al., 1998a; Nibbelke et al., 1997), but was not found for alkanes and alkenes (Padeste & Baiker, 1994; Diwell et al., 1991; Whittington et al., 1995) at low temperatures. Apparently a bifunctional path is involved when the component to be oxidised is strongly adsorbed on the noble metal. In this study, a bifunctional path for acetylene was added to the model in two ways, similar to step 2. Step 3A describes a reaction between acetylene on the noble metal with oxygen on the ceria to give 2 adsorbed CO molecules on the noble metal and gaseous water. If one of the carbon monoxide molecules produced by the bifunctional path would be released into the gas phase (table 4.2, step 3B), instead of on the noble metal, it was found that a somewhat better description of the experimental data could be obtained, which could be ascribed to a lack of vacant sites on the noble metal. The differences, however, are small. If the additionally required vacant site for step 3A would be included in the rate equations of model A, no satisfactory fit of the experimental data could be acquired.

Table 4.2. (left): Reaction steps considered for the kinetic models A and B. Two possible steps 3A and 3B were evaluated.

<table>
<thead>
<tr>
<th>Step</th>
<th>Reaction</th>
<th>Rate Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$C_2H_2 + * \rightarrow C_2H_2*$</td>
<td>$k_1^f$</td>
</tr>
<tr>
<td>2</td>
<td>$C_2H_2^* + 3O^* \rightarrow 2CO^* + H_2O + 2^*$</td>
<td>$k_{2a,b}^f$, $k_{2a}^f$, $k_{2b}^f$</td>
</tr>
<tr>
<td>3A</td>
<td>$C_2H_2^* + 3O^* + * \rightarrow 2CO^* + H_2O + 3^*$</td>
<td>$k_{3a}^f$</td>
</tr>
<tr>
<td>3B</td>
<td>$C_3H_2^* + 3O^* \rightarrow CO^* + CO + H_2O + 3^*$</td>
<td>$k_{3b}^f$</td>
</tr>
</tbody>
</table>

As mentioned before, only the rate parameters of steps 2 and 3 have been estimated by multi-response non-linear regression of the data with the complete model. The influence of the temperature has been taken into account via the Arrhenius equation. It turned out that the Arrhenius parameters for step 2 could not be determined in a statistically significant way. Therefore, this step was assumed to be not activated in the investigated temperature range. This way, all three remaining kinetic rate parameters could be determined with statistical significance. The parameters are displayed in table 4.3. Step 3B provides a slightly better description, as expressed by the confidence intervals and the F-test.

The results of the model with step 3B can be seen in figures 4.1 to 4.3 as the plotted curves. Figure 4.4 shows a parity diagram of all 105 experimental acetylene conversions and the selectivities to CO. It appears that the model is able to describe the experimental data both
According to the model, the fractional acetylene surface coverage is almost constant along the reactor axis at a value of 0.98, for the conditions \( T = 523 \text{ K}, W = 0.92 \text{ g catalyst}, F^0 = 5.6 \text{ mmol s}^{-1} \) and inlet partial pressures of 0.55 kPa oxygen and 0.15 kPa acetylene. The coverage of noble metal oxygen is about 0.013 and the coverage of the OSC (ceria) equals 0.94. With a coverage of \( 2 \times 10^{-5} \) there is hardly any CO on the surface. The OCO coverage (Nibbelke et al., 1998a) rises with the reactor axis from 0 to 0.01 through re-adsorption of desorbed CO onto noble metal oxygen. At 543 K, the oxygen adatom coverage has a value of 0.035, while the acetylene coverage remains more or less the same at a value of 0.95. This explains the influence of temperature on the CO selectivity, as mentioned before. A sensitivity analysis on the various net production rates of acetylene to carbon monoxide indicates that at low oxygen inlet partial pressures, the bifunctional path (table 4.2, step 3) is dominant. At higher oxygen inlet partial pressures, the Langmuir-Hinselwood path (table 4.2, step 2) becomes more important. This effect can be explained by the absence of adsorption competition between oxygen on the ceria and acetylene on the noble metal. It allows oxygen adsorption at low oxygen inlet partial pressures, while the adsorption rate of oxygen on the noble metal is very low, compared to the corresponding rate of acetylene adsorption.

4.4. Transient kinetics of acetylene oxidation

4.4.1. Experimental results and discussion

4.4.1.1. Transient oxidation of acetylene experiments

During the experiments, typically one feed contained 0.5 vol. % oxygen in helium (lean feed), while the other feed contained 0.15 vol. % acetylene in helium (rich feed). A reactor inlet signal, i.e. measured just in front of the catalyst bed, at an oscillation frequency of 1/20 Hz is shown in figure 4.5A. The signals of both acetylene and oxygen can be considered as
square waves, which overlap each other for approximately 0.3 s. The corresponding outlet signals of acetylene and oxygen (i.e. measured just behind the catalyst bed) at 523 K are plotted in figure 4.5B, while the measured carbon dioxide outlet signal is shown in figure 4.5C. At the specified inlet conditions and at 523 K, it was found that the time average acetylene conversion increases linearly with the oscillation frequency at least up to 1/6 Hz. This is common for hydrocarbons (Muraki et al., 1985; Silveston, 1995). The optimal duty cycle equals 50%, but the curve of the acetylene conversion versus the duty cycle is not symmetrical: the acetylene conversion at a duty cycle of 10% (i.e. acetylene is fed during 10% of the total period, while oxygen is fed during 90% of the time) is approximately three times higher than the conversion at a duty cycle of 90%. Clearly, a large excess of oxygen is beneficial for converting acetylene, as is to be expected (Bart et al., 1992; Palmer, 1975). Only a very small amount of carbon monoxide was observed during the acetylene half-cycle. The role of carbon monoxide in the acetylene oxidation has been investigated separately in section 4.3. by means of the steady state kinetic study. By varying the reactor space time, it was found that carbon monoxide is the only primary product in the oxidation of acetylene.

This means that acetylene is first converted to carbon monoxide, which reacts consecutively to carbon dioxide. Carbon monoxide has been reported often as an intermediate product in acetylene oxidation (Palmer, 1975; Megiris et al., 1985).

Before the switch from the rich to the lean feed is made, the noble metal surface is fully covered by adsorbed acetylene species, as the only reactant present in the gas phase is acetylene. When the switch is made, the feed of acetylene is replaced by the feed of oxygen (figure 4.5A), which will adsorb onto the ceria and the vacant sites of the noble metal. The fraction of vacant sites will be very low, because of the presence of surface acetylene. However, as soon as oxygen has reached the noble metal, the surface reaction will proceed, yielding water and carbon dioxide in the gas phase (figure 4.5C), as well as more vacant sites on the noble metal, available for oxygen. Hence, the production of carbon dioxide shows a sharp rise initially. As the amount of acetylene on the surface decreases, the reaction slows down and the carbon dioxide outlet concentration passes through a maximum value. Thereafter the remainder of the surface acetylene is oxidised. However, when most of the surface species have been converted, the carbon dioxide signal shows a bend, leading to a slower decrease of the outlet concentration with time. This indicates that another, more stable, surface species is being oxidised. Similar phenomena were observed for the transient oxidation of ethylene (Chapter 3). Therefore two different acetylene species seem to exist on the surface which can be converted into each other. Each shows a different oxidation behaviour. The same was found by Kesmodel et al. (1977) and Reid et al. (1973), who reported the presence of stable and less stable adsorbed acetylene on noble metal surfaces. Finally, in figure 4.5C, after all acetylene species have been oxidised, the carbon dioxide outlet concentration reaches zero, and the oxygen outlet concentration reaches its inlet level.

When the switch from lean to rich is made (e.g. at t = 12 s in figure 4.5), oxygen adatoms are converted by the adsorbing acetylene. Figure 4.5B shows that the acetylene conversion remains complete for approximately 1 second (e.g. t = 11-12 s), while carbon dioxide is formed immediately after the switch. This indicates that acetylene is able to adsorb directly on a surface, covered with oxygen, as was observed before (Dannetun et al., 1986; Palmer, 1975). Furthermore, the CO₂ peak, at the switch from oxygen to acetylene, has a much lower area than the CO₂ peak in the lean half-cycle. The difference cannot be ascribed fully to the reaction stoichiometry \( \text{C}_2\text{H}_2 + 2.5\text{O}_2 \rightarrow 2\text{CO}_2 + \text{H}_2\text{O} \). Further elaboration on this point is described in Section 4.4.3.
Shortly after the breakthrough of the acetylene at the end of the reactor, the reaction stops because the oxygen source has been depleted; the carbon dioxide concentration approaches zero and the acetylene concentration reaches its reactor inlet level. This all occurs quite early in the acetylene half-cycle. Therefore a low duty cycle (less acetylene, more oxygen) is more beneficial for the time average conversion, than a high duty cycle, as the last inactive part of the acetylene period is omitted.

The influence of the presence of ceria in the catalyst on acetylene oxidation has been tested by performing the same experiments over a Pt/$\gamma$-Al$_2$O$_3$ catalyst from the same supplier. It was seen that the CO$_2$ peak, at the switch from rich to lean, was lower but with a wider tail. The CO$_2$ peak, at the switch from lean to rich, was smaller and narrower. Also the oxygen outlet signal showed a large break through peak (Nibbelke et al., 1998a; Hoebink et al., 1999; Chapter 3). These results indicate that the presence of ceria has a significant influence on the oxidation of acetylene, although it is possible that this influence could be solely caused by the bifunctional path of the carbon monoxide oxidation (Nibbelke et al., 1998a; 1997). From the experimental data, however, a direct reaction between acetylene, adsorbed on the noble metal, and oxygen on the ceria seems significant. After the switch from rich to lean, when the noble metal surface is fully covered with acetylene, oxygen can adsorb immediately onto the catalyst with ceria, contrary to its adsorption onto the catalyst without ceria, while no acetylene desorption was observed. This is concluded from the observation of a breakthrough peak in the oxygen signal of the catalyst without ceria, in contrast to the signal with the ceria containing catalyst. The availability of oxygen on ceria leads to a high and narrow CO$_2$ peak after the rich-to-lean switch. As the ceria containing catalyst also showed a larger CO$_2$ peak after the lean-to-rich switch, when compared to the catalyst without ceria, it can be concluded that oxygen from ceria is involved in the acetylene oxidation. Generally, the influence of ceria as a provider for oxygen for hydrocarbon oxidation was found to be negligible at temperatures below 573 K (Padeste and Baiker, 1994; Diwell et al., 1991; Wittington et al., 1995; Trovarelli, 1996). Notably alkanes and alkenes were studied in this respect, but for acetylene in particular the effect of ceria was unknown up to now.

At higher temperatures, the CO$_2$ peak at the time of the switch from rich to lean is higher and has a larger area. This indicates that more acetylene species are present on the noble metal surface because of a more favourable ratio between reactive and less reactive acetylene species than at lower temperatures. As the area of the small CO$_2$ peak is almost fully determined by the amount of available oxygen on the catalyst and the reaction stoichiometry, it is weakly temperature dependent.

4.4.1.2. Simultaneous transient oxidation of acetylene and carbon monoxide

Figure 4.6A shows a reactor inlet signal, similar to the inlet signal form figure 4.5A, but in this case with 0.1 vol. % carbon monoxide added to the (rich) acetylene feed. The corresponding outlet signals, at 523 K, are displayed in figures 4.6B (acetylene, oxygen and carbon monoxide) and 4.6C (carbon dioxide).

Comparing figure 4.6 with figure 4.5, it can be seen that the oxygen outlet signals do not differ much. In the case when carbon monoxide is present, only slightly more oxygen is consumed during the lean half-cycle. The corresponding CO$_2$ peak, when switching from rich to lean, is similar to the large CO$_2$ peak in the absence of carbon monoxide in the rich feed, figure 4.5C, although it is somewhat larger, indicating that only some carbon monoxide
Figure 4.5: a. Measured reactor inlet concentrations of oxygen and acetylene versus time at an oscillation frequency of 1/20 Hz.
b. Reactor outlet concentrations of oxygen and acetylene (markers: measured data points; curves: model predictions) versus time at a temperature of 523 K and an oscillation frequency of 1/20 Hz. (note that individual data points occasionally merge into continuous lines)
c. Reactor outlet concentrations of carbon dioxide (markers: measured data points; curves: model predictions) versus time at a temperature of 523 K and an oscillation frequency of 1/20 Hz. (Note the different vertical scale)

Figure 4.6: a. Measured reactor inlet concentrations of oxygen, carbon monoxide and acetylene versus time at an oscillation frequency of 1/20 Hz.
b. Reactor outlet concentrations of oxygen, carbon monoxide and acetylene (markers: measured; curves: model predictions) versus time at a temperature of 523 K and an oscillation frequency of 1/20 Hz.
c. Reactor outlet concentrations of carbon dioxide (markers: measured; curves: model predictions) versus time at a temperature of 523 K and an oscillation frequency of 1/20 Hz. The dotted vertical line indicates the time value that applies for figures 4.8 and 4.9.
oxidation occurs early in the lean period. From the small difference between the lean periods of figures 4.5 and 4.6, it can be concluded that the presence of carbon monoxide hardly influences acetylene oxidation. Apparently, the noble metal surface is almost completely covered with acetylene species at the start of the lean period.

When the switch from lean to rich is made, it can be seen (figure 4.6B) that both acetylene conversion and carbon monoxide conversion are complete for approximately 1 s. Both reactants break through at the end of the reactor at the same time (e.g. 11.5 s). It is known that carbon monoxide (Nibbelke et al., 1998a), like acetylene (Dannetun et al., 1986; Palmer, 1975), is able to adsorb directly onto an oxygen covered surface in an Eley-Rideal-like step, as expressed by the immediate production of carbon dioxide. Both steps are important at the beginning of the rich period, because they compete for noble metal oxygen adatoms. Thereafter, both C2H2 and CO signals swiftly relax towards the corresponding inlet concentrations. The only difference with the acetylene signal in the case of acetylene-only-oxidation is that the current signal relaxates slightly faster. It indicates again that some of the oxygen adatoms are consumed in parallel by carbon monoxide. The majority of vacant sites, created by oxidation reactions, will be immediately covered by the much faster adsorbing acetylene, leaving hardly any room for carbon monoxide coverage in the rich period. Again, this shows that the acetylene oxidation is slightly influenced by the presence of carbon monoxide. This is in glaring contrast with carbon monoxide oxidation, which is almost completely inhibited by acetylene. Only direct adsorption of carbon monoxide on oxygen adatoms, leading to carbon dioxide, occurs in a significant way. The difference in stoichiometry causes the larger CO2 peak during the rich half-cycle in figure 4.6C, when compared to figure 4.5C: acetylene requires five times more oxygen than carbon monoxide.

The inhibitive effect of acetylene (Bart et al. 1992; Mabilon et al., 1995; Amon-Meziere, 1995) is even more striking when it is considered that carbon monoxide, in the absence of acetylene, can already be easily oxidised over this catalyst at temperatures around 450 K (Nibbelke et al., 1998a). Direct evidence for cross desorption processes, as is reported by Cider and Schöön (1991) and found in Chapter 3, was not found here. This is probably due to the presence of oxygen adatoms, onto which both acetylene and carbon monoxide can adsorb and react. In the case of Cider and Schöön, oxygen was not present on the catalyst surface, while ethylene (Chapter 3) lacks the ability to adsorb onto oxygen adatoms. In these cases competition for vacant noble metal sites, which could lead to cross desorption, is important.

4.4.2. Kinetic modelling of the transient acetylene oxidation

The measured kinetic responses have been modelled in a similar way as to that described by Nibbelke et al. (1998a) and in Chapter 3. The objective of the modelling work is to construct a transient kinetic model, based on relevant elementary steps, which presents an adequate description of the measured C2H2, O2, CO, and CO2 concentrations in time at the reactor outlet for specified inlet conditions.

4.4.2.1. Reactor model equations

The fixed-bed reactor is regarded as an ideal isothermal plug flow reactor, with a constant total molar flow rate along the catalyst bed. The model consists of the continuity equations for 1) C2H2, O2, CO, and CO2 in the gas phase, 2a) surface species adsorbed on the noble metal surface,
2b) CO₂ adsorbed on the γ-Al₂O₃ support,
2c) oxygen adsorbed on the oxygen storage capacity (OSC) of ceria.

The continuity equation for gas phase component \( i \) is as follows:

\[
\frac{\partial C_i}{\partial t} + \frac{1}{\tau} \frac{\partial C_i}{\partial z} = \sum_k L_k R_{k,i} \tag{4.8}
\]

The continuity equations for species \( j \) adsorbed on the noble metal surface, species \( n \) on the alumina support, and species \( m \) on the ceria surface can be written as follows:

\[
L_{NM} \frac{\partial \theta_j}{\partial t} = \sum_k L_k R_{k,j} \tag{4.9a}
\]

\[
L_{SUP} \frac{\partial \delta_n}{\partial t} = \sum_k L_k R_{k,n} \tag{4.9b}
\]

\[
L_{OSC} \frac{\partial \xi_m}{\partial t} = \sum_k L_k R_{k,m} \tag{4.9c}
\]

As the initial condition for Equations (4.8) and (4.9), the steady state solution corresponding to the experimental conditions during the rich feeding half cycle, i.e. 0.15 mol % C₂H₂ (plus 0.10 mol % CO if relevant) in helium at reaction temperature, was chosen. The boundary condition for Equation (4.8) is:

\[
z = 0, \ t > 0, \ C_i = C_i^0(t) \tag{4.10}
\]

The experimentally measured reactor inlet concentrations were used to produce model predictions for the outlet responses. The reactor inlet concentrations of CO₂ and H₂O were always kept zero.

The net production rates in Equations (4.8) and (4.9) can be calculated from the rates of the elementary reaction steps in the reaction mechanism, considered in section 4.4.2.4.:

\[
R_{k,j} = \sum_p v_{i,p} r_{k,p} \tag{4.11}
\]

The reaction rates \( r_{k,p} \) of the elementary reaction steps are calculated via the law of mass action while restricting the adsorption capacity to a monolayer as a maximum.

Since the calculations started from the steady state solution as initial condition, they had to be carried out until a stable periodic solution was reached. The latter was usually the case after one cycling period.

### 4.4.2.2. Numerical calculations

A backward differentiation formula, BDF, integrator from the NAG Fortran library Mark 18, (1997), routine D02NHF, was used for calculating the steady state solution of Equations (4.8) and (4.9).

The transient calculations were carried out using the Method of Lines (Schiesser, 1991). This method consists of discretisation of the space-derivatives by finite differences. The set of partial differential equations becomes a set of ordinary differential equations, ODE, which can be integrated in time by an ODE integrator. The first order space-derivatives, i.e. the convection terms in Equation (4.1), were discretised by so-called backward or upstream differentiation. The time-integration was carried out using a BDF integrator from the NAG Fortran library (NAG, 1997), routine D02NCF. The numerical calculations were carried out on a Silicon Graphics CRAY Origin2000. A typical CPU time for simulating two periods amounts 120 s.
4.4.2.3. Regression analysis

Estimation of the kinetic parameters was performed with a non-linear multi-response regression analysis of the C$_2$H$_2$, O$_2$, and CO$_2$ outlet concentrations. The following objective function was minimised:

$$S(b) = \sum_{q=1}^{v} \sum_{i=1}^{n} w_{i,q} [y_{i,q} - g_q(x_i, b)]^2 \rightarrow \text{minimum}$$

(4.7)

The function represents the weighted sum of squares for all measured gas phase concentrations over the entire experimental time, except for the first, unstable, cycle. Minimisation was achieved with a multi-response Levenberg-Marquart algorithm (Froment & Hosten, 1981; Boggs et al., 1992). The regression of the transient acetylene oxidation data was carried out at a frequency of 1/20 Hz at temperatures of 503, 523 and 543 K. The three independent data sets contain a total of 4797 experimental data points. All weight factors were set to unity. The frequency of 1/20 Hz was chosen, as it allows relaxation of all observed signals towards the quasi-steady state levels.

4.4.2.4 Reaction mechanism

On the basis of the experimental results, a reaction scheme is suggested for the oxidation of acetylene. As mentioned before, carbon monoxide was found to be the only primary reaction product, implying that acetylene is first partially oxidised to carbon monoxide, which reacts consecutively to carbon dioxide. As a model, based on elementary reaction steps, is already available for carbon monoxide oxidation over this catalyst (Nibbelke et al., 1998a), it should be sufficient to extend this model with sorption and reaction steps for conversion of acetylene into carbon monoxide. The proposed sequence of reaction steps to convert C$_2$H$_2$ into adsorbed CO is presented in table 4.4. The reaction steps of the model for the transient carbon monoxide oxidation are listed in table 4.5; the values of the rate constant are not repeated here (Nibbelke et al., 1998a). This model consists of three different pathways: 1) Adsorption of carbon monoxide and oxygen on noble metal, followed by a Langmuir-Hinselwood surface reaction; 2) Adsorption of carbon monoxide on an oxygen covered site, with subsequent carbon dioxide desorption from so-called OCO species; 3) Reaction between carbon monoxide adsorbed on the noble metal and oxygen adsorbed on ceria, the so-called bifunctional path. When incorporating this model into the kinetics for C$_2$H$_2$ oxidation, all rate coefficients of the transient carbon monoxide oxidation model were used as reported (Nibbelke et al., 1998a), with the exception of the desorption coefficient of carbon monoxide. This value, determined at temperatures between 393 and 433 K, appeared too high when extrapolated to temperatures between 503 and 543 K, as used in this study. For that reason, the pre-exponential factor was changed from $5.65 \times 10^{14}$ s$^{-1}$ to $2.5 \times 10^{11}$ s$^{-1}$ and the activation energy was changed from 113 kJ/mol to 89 kJ/mol.

The mechanism to describe acetylene conversion into adsorbed CO is discussed in more detail. For the treatment of two acetylene surface species, the work of Kesmodel et al. (1977) was followed: 1) $\pi$ acetylene, adsorbed on one catalytic site (atop), is the most unstable and therefore most reactive species; 2) $\sigma$+$\mu$ acetylene, triangular adsorbed, is stable and therefore refractory towards oxidation.

The reversible adsorption of acetylene (step 1) leads to $\pi$ acetylene on the surface and is first order in the vacant sites. Although significant acetylene desorption was not detected during the experiments, acetylene is likely to desorb to some extent (Megiris et al., 1985), creating vacant sites for oxygen adsorption, especially after a switch from rich to lean. It is clear that the desorption coefficient should be low at the temperatures considered. Step 2 describes the reversible conversion of the two types of adsorbed acetylene into each other.
Table 4.4. Elementary steps considered in the kinetic modelling of the transient acetylene oxidation by oxygen over Pt/Rh/CeO$_2$/$\gamma$-Al$_2$O$_3$. The model holds in combination with the CO oxidation model of Table 4.5.

<table>
<thead>
<tr>
<th>Step no.</th>
<th>Elementary reaction step</th>
<th>Reaction path</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>A</td>
</tr>
<tr>
<td>1</td>
<td>C$_2$H$_2$ (g) + *</td>
<td>$k_1^f$</td>
</tr>
<tr>
<td>2</td>
<td>C$_2$H$_2^<em>$ + 2</em></td>
<td>$k_2^f$</td>
</tr>
<tr>
<td>3</td>
<td>C$_2$H$_2^<em>$ + 3O</em></td>
<td>$k_3^f$</td>
</tr>
<tr>
<td>4</td>
<td>C$_2$H$_2^{**<em>}$ + 3O</em></td>
<td>$k_4^f$</td>
</tr>
<tr>
<td>5</td>
<td>C$_2$H$_2$ (g) + O*</td>
<td>$k_5^f$</td>
</tr>
<tr>
<td>6</td>
<td>C$_2$H$_2$O* + 2O*</td>
<td>$k_6^f$</td>
</tr>
<tr>
<td>7</td>
<td>C$_2$H$_2^*$ + 3Os</td>
<td>$k_7^f$</td>
</tr>
</tbody>
</table>

\[ C_2H_2 + 2.5 O_2 \rightarrow 2CO_2 + H_2O \]

The conversion of $\pi$ acetylene to di-$\sigma$+$\mu$ ethylene requires two vacant sites, making the latter species less abundant when acetylene is in the gas phase (rich period). The rate of this step is second order in the fraction of vacant sites. The direct partial combustion of both acetylene species to adsorbed carbon monoxide is described by steps 3 and 4, i.e. reaction paths A and B. Although not elementary, the first and rate determining step is assumed to be the oxygen assisted abstraction of the weakest bonded hydrogen atom (Amon-Meziere et al., 1995; Palmer, 1975; Mate et al., 1988), whereupon oxidation to carbon monoxide occurs instantaneously. Decomposition of acetylene on the surface is unlikely because of the small number of vacant sites, and the relatively large molar flow rates in the reactor.

Steps 5 and 6 show an Eley-Rideal type of reaction path (path C) for the combustion of acetylene. As mentioned before, acetylene is able to adsorb on an oxygen-covered surface to yield oxidation products immediately (Dannetun et al., 1986; Palmer, 1975). Therefore, the species formed in step 5, is believed to be highly unstable and will react rapidly through step 6 to adsorbed carbon monoxide.

Step 7, finally, describes the influence of ceria in the catalyst on the oxidation of acetylene through a bifunctional path. Only the reaction between the $\pi$ acetylene and the ceria oxygen has been used in the model.
Table 4.5. Elementary steps considered in the kinetic modelling of the transient carbon monoxide oxidation by oxygen over Pt/Rh/CeO$_2$/$\gamma$-Al$_2$O$_3$ as reported by Nibbelke et al. (1998a).

<table>
<thead>
<tr>
<th>Step nr.</th>
<th>elementary reaction steps</th>
<th>reaction path</th>
<th>$\sigma_A$</th>
<th>$\sigma_B$</th>
<th>$\sigma_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>CO $+ \ast$ $\xrightarrow{k_8^f}$ CO$\ast$</td>
<td></td>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>9</td>
<td>O$_2$ $+ \ast$ $\xrightarrow{k_9^f}$ O$_2\ast$</td>
<td></td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>O$<em>2\ast$ $+ \ast$ $\xrightarrow{k</em>{10}^f}$ 2 O$\ast$</td>
<td></td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>CO$\ast$ $+ O\ast$ $\xrightarrow{k_{11}^f}$ CO$_2$ $+ 2 \ast$</td>
<td></td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>CO $+ O\ast$ $\xleftarrow{k_{12}^f}$ OCO$\ast$</td>
<td></td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>OCO$\ast$ $\xrightarrow{k_{13}^f}$ CO$_2$ $+ \ast$</td>
<td></td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>14</td>
<td>O$<em>2$ $+ s$ $\xrightarrow{k</em>{14}^f}$ O$_2s$</td>
<td></td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>15</td>
<td>O$<em>2s$ $+ s$ $\xrightarrow{k</em>{15}^f}$ 2 Os</td>
<td></td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>16</td>
<td>CO$\ast$ $+ Os$ $\xrightarrow{k_{16}^f}$ CO$_2$ $+ \ast$ $+ s$</td>
<td></td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td>17</td>
<td>CO$<em>2$ $+ \gamma$ $\xleftarrow{k</em>{17}^f}$ CO$_2\gamma$</td>
<td></td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2 CO $+ O_2$ $\longrightarrow$ 2 CO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.4.3. Selective deactivation

During the modelling work, it appeared impossible to explain just by stoichiometry the difference between the large CO$_2$ peak, when switching from acetylene to oxygen, and the small CO$_2$ peak, when switching from oxygen to acetylene. Apparently the catalyst’s sorption capacity for acetylene is larger than for oxygen. The same effect was also found for transient ethylene oxidation (Chapter 3), where a selective deactivation for oxygen was included in the model, leading to a maximum fractional oxygen coverage that is below unity. As an explanation, it was assumed that carbonaceous deposits from ethylene were deposited, which is known to occur (Berlowitz et al., 1985; Kvon et al., 1998). Also in the case of acetylene, formation of carbonaceous deposits has been observed (Dannetun et al., 1986; Palmer, 1975; Megiris et al., 1985, Reid et al., 1973; Ibach et al., 1978). Elemental analysis, in the present work, showed that the used catalyst contained 1.2 wt % carbon. This deposition took place within the few hours of time-on-stream, while afterwards the catalyst showed a stable activity for at least three weeks. For the current modelling work, a carbonaceous layer was taken into account in the model equations by assuming that a constant fraction of the noble metal capacity is unavailable for oxygen only. The value of this fraction was determined using regression to be 0.59. This value is in the same order of magnitude as was found in the LEIS study, described in section 3.7. The rate constants for acetylene adsorption and reaction on the carbonaceous layer was assumed to be the same as on the noble metal. Furthermore, the carbonaceous matter was assumed to be equally distributed over the entire noble metal surface.
4.4.4. Kinetic model equations

The fractions of vacant sites on the noble metal, on the carbonaceous deposits, and on the OSC (ceria) are defined as:

\[
\theta_s = 1 - \theta_c - \theta_{C,H_2}* - \theta_{C,H_2}*** - \theta_{CO} - \theta_{C,H_2}O* - \theta_{CH_s}
\]  
(4.12)

\[
\theta_C = \theta_{CH_s} - \theta_{C,H_2}* - \theta_{C,H_2}*** - \theta_{CO}^C
\]  
(4.13)

\[
\xi_O = 1 - \xi
\]  
(4.14)

All fractions are defined as the number of metal sites occupied by the specific species, relative to the total number of available metal sites. In this way the coverage of \(\pi\) acetylene, for instance, includes \(\pi-\)adsorbed acetylene on noble metal and on noble metal covered by a carbonaceous layer.

The production rates for the gas phase components in equation (4.8) become:

\[
\sum_k L_k R_{k,C,H_2} = L_{NM}(-k_f^f C_{C,H_2} (\theta_c + \theta_C^C) + k_f^{C} (\theta_{C,H_2}* + \theta_{C,H_2}*** - k_f^f C_{C,H_2} \theta_O + k_s^f \theta_{C,H_2,0})
\]  
(4.15)

\[
\sum_k L_k R_{k,CO} = L_{NM}(-k_8^f C_{CO} (\theta_c + \theta_C^C) + k_8^b \theta_{CO}^C - k_{12}^f C_{CO} \theta_O + k_{12} \theta_{CO,O})
\]  
(4.16)

\[
\sum_k L_k R_{k,O_2} = L_{NM}(-k_9^f C_{O_2} \theta_c) + L_{OSC}(-k_{14}^f C_{O_2} \xi)
\]  
(4.17)

\[
\sum_k L_k R_{k,CO_2} = L_{NM}(k_{11}^f (\theta_{CO} + \theta_{CO}^C) \theta_O + k_{13} \theta_{CO,O} + k_7^f (\theta_{C,H_2}* + \theta_{C,H_2}** \xi_O)
\]  
(4.18)

\[
\sum_k L_k R_{k,H,O} = L_{NM}(k_7^f (\theta_{C,H_2}* + \theta_{C,H_2}**) \theta_O + k_9^f (\theta_{C,H_2}* + \theta_{C,H_2}**) \theta_O + k_{17} \theta_{CO,O})
\]  
(4.19)

The production rates of the noble metal surface species for insertion into equation (4.9) are written as:

\[
\sum_k L_k R_{k,C,H_2,*} = L_{NM}(k_1^f C_{C,H_2} \theta_s - k_s^b \theta_{C,H_2}* - k_2 \theta_{C,H_2}** + k_2^b \theta_{C,H_2}* - k_s^f \theta_{C,H_2} \theta_O
\]  
(4.20)

\[
\sum_k L_k R_{k,C,H_2,**} = L_{NM}(3k_2^f \theta_{C,H_2}^C \theta_c^2 - 3k_2 \theta_{C,H_2}** - 3k_4^f \theta_{C,H_2,**} \theta_O)
\]  
(4.21)

\[
\sum_k L_k R_{k,CO} = L_{NM}(k_8^f C_{CO} \theta_c - k_8 \theta_{CO}^C - k_{11}^f \theta_{CO} \theta_O + 2k_8^f \theta_{C,H_2} \theta_O + 2k_8 \theta_{C,H_2,**} \theta_O
\]  
(4.22)

\[
\sum_k L_k R_{k,O} = L_{NM}(2k_8^f C_{O_2} \theta_s - 3k_5^f (\theta_{C,H_2}* + \theta_{C,H_2}**) \theta_O - 3k_4^f (\theta_{C,H_2,**} + \theta_{C,H_2,**}^C) \theta_O
\]  
(4.23)

\[
\sum_k L_k R_{k,CO_2} = L_{NM}(k_9^f C_{CO} \theta_c - k_{16}^f \theta_{CO} \xi + k_9^f \theta_{C,H_2} \xi)
\]  
(4.24)

\[
\sum_k L_k R_{k,C,H_2,O} = L_{NM}(k_2^f C_{C,H_2} \theta_s - k_2^b \theta_{C,H_2,O} - k_9^f \theta_{C,H_2,0} - k_{17} \theta_{CO,O})
\]  
(4.25)
\[
\sum_{k} L_{\text{k}} R_{k,C_{2}H_{2}^{\text{f}}^{\text{c}}^{\text{f}}^{\text{c}}} = L_{\text{NM}}(k_{\text{f}}^{\text{f}} C_{C_{2}H_{2}}^{\theta} - k_{\text{f}}^{\text{f}} C_{C_{2}H_{2}}^{\theta} + k_{\text{f}}^{\text{f}} C_{C_{2}H_{2}}^{\theta} + k_{\text{f}}^{\text{f}} C_{C_{2}H_{2}}^{\theta} - k_{\text{f}}^{\text{f}} C_{C_{2}H_{2}}^{\theta} \theta_{O})
\]

\[
\sum_{k} L_{\text{k}} R_{k,C_{2}H_{2}^{\text{f}}^{\text{c}}^{\text{f}}^{\text{c}}} = L_{\text{NM}}(3k_{\text{f}}^{\text{f}} C_{C_{2}H_{2}}^{\theta} - 3k_{\text{f}}^{\text{f}} C_{C_{2}H_{2}}^{\theta} \theta_{O} - 3k_{\text{f}}^{\text{f}} C_{C_{2}H_{2}}^{\theta} \theta_{O})
\]

\[
\sum_{k} L_{\text{k}} R_{k,CO^{\text{f}}} = L_{\text{NM}}(k_{\text{f}}^{\text{f}} C_{CO}^{\theta} - k_{\text{f}}^{\text{f}} C_{CO}^{\theta} - k_{\text{f}}^{\text{f}} C_{CO}^{\theta} + 2k_{\text{f}}^{\text{f}} C_{CO}^{\theta} \theta_{O} + 2k_{\text{f}}^{\text{f}} C_{CO}^{\theta} \theta_{O})
\]

The production rate of CO\text{2} adsorbed on the support sites, \(\gamma\), surface becomes:

\[
\sum_{k} L_{\text{k}} R_{k,C_{2}H_{2}^{\text{f}}^{\text{c}}^{\text{f}}^{\text{c}}} = L_{\text{SUP}}(k_{\text{f}}^{\text{f}} C_{CO}^{\theta} - k_{\text{f}}^{\text{f}} C_{CO}^{\theta})
\]

The production rate of O adsorbed on the ceria sites, \(\xi\), surface becomes:

\[
\sum_{k} L_{\text{k}} R_{k,CO^{\text{f}}} = L_{\text{OSC}}(k_{\text{f}}^{\text{f}} C_{CO}^{\theta} - k_{\text{f}}^{\text{f}} C_{CO}^{\theta} - k_{\text{f}}^{\text{f}} C_{CO}^{\theta} - k_{\text{f}}^{\text{f}} C_{CO}^{\theta} + \frac{3k_{\text{f}}^{\text{f}} C_{CO}^{\theta} + \theta_{CO}^{\theta}}{2} \theta_{O})
\]

For all steps, adsorption rate coefficients were taken as temperature independent, whereas for surface reaction and desorption steps, the rate coefficients were related to temperature through an Arrhenius type of equation. The adsorption rate coefficient of acetylene is based on a sticking coefficient of unity, in line with literature reports (Mabilon et al., 1995; Dannetun et al., 1986; Palmer, 1977).

In the regression analysis of the acetylene oxidation responses with the combined C\(_{2}\)H\(_{2}\)/CO model, the kinetic parameters for carbon monoxide oxidation and oxygen adsorption were taken from the work of Nibbelke et al. (1998a) for the same catalyst. Also the catalyst properties, including the carbon dioxide sorption capacity of the support were taken from this study. As mentioned before, an exception was made for the carbon monoxide desorption coefficient. The noble metal capacity was determined from carbon monoxide chemisorption on a used catalyst as 12.2 mmol sites kg\(_{\text{cat}}^{-1}\). For the Oxygen Storage Capacity (OSC) of ceria, the value of 3.0 \(10^{-3}\) mol kg\(_{\text{cat}}^{-1}\), half the value used by Nibbelke et al. (1998a), had to be taken to obtain an adequate fit. This can be explained by a spill over of carbonaceous matter from the noble metal onto the OSC (Ferrizz et al., 1999). All other rate parameters of the reaction steps specified in table 4.4, as well as the fraction of carbonaceous deposits, were determined by regression.

In order to describe the combined acetylene and carbon monoxide oxidation experiments, the same model as for the acetylene-only-oxidation was used, without any adaptations. For the combined ethylene and carbon monoxide oxidation (Chapter 3), the fraction of carbonaceous matter (0.4) was different from the value for the ethylene-only-oxidation (0.66). Apparently, carbon monoxide may influence the presence of a carbonaceous layer. In the present work, no effect of carbon monoxide on the fraction of carbonaceous matter was found, which can be explained by the absence of large amounts of carbon monoxide on the surface during all experiments.

4.4.5. Modelling results of the transient acetylene oxidation

4.4.5.1 Comparison between experiments and model predictions

The kinetic rate coefficients, obtained from the regression analysis are displayed in table 4.6. The model predictions at a reactor temperature of 523 K and an oscillation frequency of 1/20
Hz are shown as drawn curves together with the measured reactor outlet signal in figures 4.5B and 4.5C. The model adequately predicts the experimental results. There are some small deviations, especially when switching from rich to lean. The model predicts a small oxygen breakthrough peak, while the experiment shows a smooth curve, however, with a point of inflection. At the same time the model predicts a delay in the decrease of the acetylene concentration, which is not seen in the experiments. Both deviations indicate that the adsorption of oxygen proceeds more easily than considered in the model. An oxygen breakthrough peak would occur when oxygen initially is unable to adsorb onto the surface due to a lack of vacant sites. This has been discussed before by Nibbelke et al. (1998a), Hoebink et al. (1999) and in Chapter 3.

4.4.5.2 Model parameter comparison

As rate parameters for acetylene oxidation are rather scarce in the literature, a comparison with the current results is hardly possible. Only sticking coefficients for acetylene near unity have been reported (Mabilon et al., 1995; Dannes et al., 1986; Palmer, 1977). This would indicate an adsorption rate coefficient of about 1 $10^7$ m$^3$ mol$^{-1}$ s$^{-1}$, which was used for the model calculations in this study. Furthermore, the rate coefficients can be compared with the theoretical work of Zhidanov et al. (1998). The pre-exponential factors of reactions 2b, 3f, and 7f are within the theoretical range ($10^{11}$-$10^{19}$ s$^{-1}$). The values of the pre-exponential factors of reactions 1b and 2f are near the lower boundary ($10^{11}$ and $10^{13}$ s$^{-1}$ respectively).

Table 4.6. Estimates of the kinetic rate parameters obtained by regression of the cyclic feeding experiments at three temperatures, i.e. 503, 523, 543 K, and a forcing frequency 1/20 Hz for the acetylene oxidation by oxygen over Pt/Rh/CeO$_2$/γ-Al$_2$O$_3$.

<table>
<thead>
<tr>
<th>$k_1$</th>
<th>$1.32 \times 10^7$ m$^3$ mol$^{-1}$ s$^{-1}$</th>
<th>$A_4$</th>
<th>$2.25 \times 10^{10}$ s$^{-1}$</th>
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<tbody>
<tr>
<td>$A_1$</td>
<td>$1.11 \times 10^{11}$ s$^{-1}$</td>
<td>$E_4$</td>
<td>161 kJ mol$^{-1}$</td>
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<tr>
<td>$E_1$</td>
<td>93.5 kJ mol$^{-1}$</td>
<td>$k_5$</td>
<td>$5.34 \times 10^{2}$ m$^3$ mol$^{-1}$ s$^{-1}$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$2.50 \times 10^9$ s$^{-1}$</td>
<td>$k_5$</td>
<td>5.86 s$^{-1}$</td>
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<tr>
<td>$E_2$</td>
<td>44.4 kJ mol$^{-1}$</td>
<td>$k_6$</td>
<td>$8.63 \times 10^3$ s$^{-1}$</td>
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<tr>
<td>$A_2$</td>
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<td>$A_7$</td>
<td>$1.76 \times 10^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$E_2$</td>
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<td>$E_7$</td>
<td>124 kJ mol$^{-1}$</td>
</tr>
<tr>
<td>$A_3$</td>
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<td>$\theta_{CH_4}$</td>
<td>0.59 -</td>
</tr>
<tr>
<td>$E_3$</td>
<td>151 kJ mol$^{-1}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The value of the pre-exponential factor of reaction 4f is very low, as to be expected for partial oxidation of refractory surface acetylene. As the values of the activation energies of steps 5b and 6f were found to be very low, these steps were thereafter assumed to be temperature independent. The value of step 6f also appeared to be quite large, indicating the instability of the related surface species, as mentioned before.

The kinetic parameters, involved in the transient carbon monoxide oxidation, were already discussed by Nibbelke et al. (1998a).
4.4.5.3 Fractional surface coverages during the acetylene oxidation

Figure 4.7 shows the model predictions of the fractional surface coverages versus time at the end of the reactor. In this figure the fraction of species adsorbed on the carbonaceous deposits have been added to the fraction of the same species on the noble metal.

At the end of the rich cycle part, e.g. at circa 21 s, the noble metal is almost fully covered with $\pi$ acetylene. At the moment of the switch, the coverage of this species starts to decrease and the coverage of oxygen adatoms starts to rise. After approximately 1 second, the di-$\sigma+\mu$ acetylene fraction also starts to rise. The $\pi$ acetylene is oxidised at first, yielding vacant sites, which are not only used for the adsorption of oxygen, but also for the formation of di-$\sigma+\mu$ acetylene from $\pi$ acetylene. This latter process requires two vacant sites per acetylene molecule, and therefore only occurs when a relative large fraction of vacant sites is present. Also, this di-$\sigma+\mu$ acetylene species is quite refractory towards oxidation, so it will be able to exist next to oxygen on the surface. Carbon monoxide produced from acetylene is oxidised so fast, that no significant carbon monoxide coverage is predicted (the carbon monoxide coverage at the end of the reactor does not exceed $3.0 \times 10^{-3}$). However, some carbon monoxide can desorb from the surface and re-adsorb onto oxygen adatoms to form OCO species, that will desorb as carbon dioxide. When more oxygen becomes present on the surface, carbon monoxide is oxidised before desorption and hence the OCO disappears quickly. As the lean cycle part proceeds, all $\pi$ acetylene is converted into CO$_2$ via CO and into di-$\sigma+\mu$ acetylene. The latter species accumulates on the surface. The oxygen vacancies on ceria are gradually filled during the lean part of the period, which demonstrates the positive effect of ceria in oxidising acetylene. The slower relaxation towards unity indicates that the bifunctional reactions proceed slower than the noble metal reactions. There is a disturbance in $\xi_O$ around 22 s, which probably is related with carbon monoxide oxidation via the bifunctional path. At the end of the lean half cycle, the noble metal surface is occupied by the slowly reacting di-$\sigma+\mu$ acetylene species and oxygen adatoms. The oxygen storage capacity (ceria) is completely filled.

After the switch to the rich conditions has been made, oxygen from the noble metal is quickly depleted and thereafter the oxygen from ceria is consumed rapidly. Again some carbon monoxide desorbs and re-adsorbs as OCO species, which disappear more quickly than when
switching from rich to lean, due to fast oxygen consumption. The conversion from di-σ+μ
cetylene to the π version is favoured more than the reverse reaction, as vacant sites are
immediately filled by adsorbing π acetylene. Hence, the surface will again be replenished
with π acetylene until the switch to the lean conditions is made again.

4.4.6. Modelling results of the simultaneous acetylene and carbon monoxide oxidation

4.4.6.1 Comparison between experiments and model predictions

The model predictions of the combined acetylene and carbon monoxide oxidation are
compared with experiments in figures 4.6B and 4.6C, at a temperature of 523 K and an
oscillation frequency of 1/20 Hz. Again, the model is well able to predict the experimental
data. The minor deviations are similar to those for acetylene-only-oxidation.

The predicted fractional coverages versus time at the end of the reactor are similar to those
for the model predictions of the experiment where carbon monoxide was not added to the
feed (figure 4.7). As was explained before, CO oxidation via OCO is the major reaction path
when acetylene is present, since the carbon monoxide coverage is very low during the entire
experiment. After the switch from rich to lean, more OCO species are formed in the case
where carbon monoxide was added to the feed. The OCO coverage, however, is small
compared to the acetylene coverages, and the OCO presence does not significantly influence
the acetylene oxidation, as was also concluded from the experiments. At the switch from lean
to rich, suddenly a small jump in the coverage of di-σ+μ acetylene is predicted. After this, the
coverage decreases slowly, as in the acetylene-only-experiments. This causes the maximum
of the π acetylene at the end of the rich period to be slightly lower. In order to explain this
phenomenon, a cross section along the reactor axis must be considered, as will be done in the
next paragraph.

4.4.6.2 Reactor profiles during the simultaneous acetylene and CO oxidation

In figures 4.8 and 4.9 respectively the model predicted concentration profiles and fractional
coverage profiles are plotted versus the reactor axis at t = 31.5 s. This particular time is after
the switch from lean to rich, but before the break through of the acetylene and carbon
monoxide signals (see vertical dotted line in figure 4.6C). Figures 4.8 and 4.9 are presented
for a better understanding of the mutual influence of acetylene and carbon monoxide
oxidation. Figure 4.8 shows that gaseous oxygen is not present in the reactor, and that the
conversions of both CO and C₂H₂ are complete at the end of the reactor. At approximately
x = 11.5 mm, the concentrations of CO and C₂H₂ reach zero rather abruptly, causing a large
rise of the carbon dioxide concentration. This corresponds with a major consumption of
oxygen on the noble metal, as can be seen at the same position in figure 4.9. Apparently, a
reaction front moves through the reactor with time, consuming all noble metal oxygen.
Upstream of this front the acetylene concentration decreases gradually along the reactor axis.
As in this part of the reactor (0 < x < 12 mm) noble metal oxygen is almost absent, the
conversion of acetylene proceeds mainly via the bifunctional path, as indicated by the gradual
increase of the OSC coverage (figure 4.9) and the decrease of the π acetylene coverage. Since
the oxidation provides empty sites, part of the π acetylene is transformed into di-
σ+μ acetylene, the coverage of which increases as well. The latter also holds for the OCO
coverage, caused by some adsorption of fed CO and re-adsorption of CO, previously
desorbed after being formed from acetylene, on noble metal sites, still covered with oxygen adatoms. Desorption of product carbon monoxide is also reflected by the carbon monoxide gas phase concentration, which increases along the reactor axis in the front part of the reactor (figure 4.8), up to levels that exceed the carbon monoxide feed concentration. This behaviour is due to competitive adsorption, also called cross desorption, as already observed for acetylene, ethylene, and carbon monoxide by Cider and Schöön (1991).

Between the positions at $x = 8$ and $x = 12.5$ mm in the reactor, a peculiar phenomenon is noticed: a higher level of the di-$\sigma+\mu$ acetylene surface coverage accompanied by a lower level of the $\text{OCO}^*$ fraction. This phenomenon was not found during the simulations of the transient oxidation of acetylene without carbon monoxide feeding. Furthermore, it was found to occur only on noble metal sites which were not covered by carbonaceous deposits. The phenomenon therefore seems likely to be involved with $\text{OCO}^*$ species formed from gaseous carbon monoxide and existing only on the noble metal sites. The model predicted the higher level of the di-$\sigma+\mu$ acetylene fraction at $t = 31.25$ s and $x = 7.7$ mm, i.e. the location of the reaction front at that time. This indicates that the formation of the higher level of the di-$\sigma+\mu$ acetylene coverage is located in the reaction front. From then on, the phenomenon expands in the direction of the reactor axis with time, following the reaction front. At the location of the reaction front, the gas phase carbon monoxide concentration exceeds the gas phase concentration of acetylene, while also the coverage of $\text{OCO}^*$ exceeds the coverage of $\text{C}_2\text{H}_2^*$ on the noble metal (excluding its coverage on the carbonaceous deposits), a situation which is unique for approximately $0.1$ s. Before and after this period, the situation is reversed.

![Figure 4.8. Model predicted gas phase concentrations versus the reactor co-ordinate, at 31.5s during the experiment displayed in figure 4.6.](image)

According to the model, the only possible way to create the di-$\sigma+\mu$ acetylene on the surface is through reaction step 2f (table 4.4), which requires two vacant sites on the surface, next to $\pi$ acetylene, which is abundantly present in the front part of the reactor. This means that di-$\sigma+\mu$ acetylene can only be formed when sufficient vacant sites are present on the surface. This is exactly the case at the location of the reaction front in the reactor, because of the fast reactions taking place there, yielding many vacant sites available for di-$\sigma+\mu$ acetylene production. The backward reaction step 2b (table 4.4) is very slow, so the higher coverage level expands in length.
The question is now why the supply of additional gaseous carbon monoxide at the reactor inlet would lead to a higher fraction of vacant sites at the reaction front. When no additional carbon monoxide is fed to the reactor, less OCO* is predicted, which seems reasonable as OCO* is formed from gaseous carbon monoxide.

The gas phase carbon monoxide concentration increases along the reactor axis, whether carbon monoxide is fed or not. The way, however, that carbon monoxide concentration reaches zero at the reaction front, is completely different: in the absence of additional carbon monoxide, its concentration decreases rather gradually, but with extra carbon monoxide present, its concentration drops suddenly at the reaction front (figure 4.8). This is in line with the large formation of carbon dioxide in the gas phase (compare figure 4.5C with figure 4.6C at t = 31 s).

In the first part of the reactor, hardly any CO* and O* are present on the surface, as the surface is almost fully covered with acetylene species. These are slowly converted (e.g. by the bifunctional path) yielding carbon monoxide, which partly desorbs, leading to an increasing gas phase carbon monoxide concentration along the reactor axis. At the location of the reaction front, suddenly O* is available. Apparently, the concentration of gaseous carbon monoxide determines the desorption rate of OCO* species, which can occur in two ways: 1) desorption as CO₂, yielding vacant noble metal sites (step 13, table 4.5: OCO* → CO₂ + *); 2) desorption as CO and O* on the noble metal surface (step 12b, table 4.5: OCO* → CO + O*).

The first way seems to be the most important one, considering the massive production of CO₂. The second way (step 12f, table 4.5: CO + O* → OCO*) would seem to be faster than step 12b, as both gaseous carbon monoxide and oxygen adatoms are present at this time and location. Apparently, the sudden presence of oxygen adatoms on the noble metal and CO in the gas phase cause a fast desorption of OCO* as CO₂, leading to vacant sites, which are used by the formation of di-σ+µ acetylene.

The location in the reactor where this phenomenon starts depends on the carbon monoxide inlet concentration; if higher carbon monoxide concentrations in the feed were used for the simulation, the phenomenon would be more pronounced and occur at a location nearer to the
inlet of the reactor. Apparently, there is a critical carbon monoxide inlet concentration, leading to a critical OCO coverage, needed for the occurrence of the described phenomenon at the reaction front.

4.5. Conclusions

The steady state oxidation of acetylene with oxygen over a commercially available Pt/Rh/CeO$_2$/γ-Al$_2$O$_3$ three-way catalyst has been investigated at cold-start conditions. It was found that the partial reaction order is negative for acetylene and positive for oxygen. Increasing the temperature led to a higher conversion of acetylene and a lower selectivity to CO. Carbon monoxide was found to be the only primary reaction product, which may be oxidised to CO$_2$ consecutively. A kinetic model for the partial oxidation of acetylene to carbon monoxide has been developed, which was added to the published kinetics for CO oxidation over the same catalyst (Nibbelke et al., 1998a). The combined model is able to predict the experimental results quite adequately. The adsorption rate coefficient for acetylene was derived from literature, while a low rate of acetylene desorption was used. Rate parameters for the direct conversion of acetylene to adsorbed carbon monoxide by oxygen on both noble metal and ceria have been obtained by regression.

The transient oxidation of acetylene over a three-way catalyst has been studied for automotive cold start conditions. Feed cycling experiments with oxygen and acetylene indicate the presence of two different acetylene surface species, which were ascribed to reactive π acetylene and refractory di-σ+µ acetylene. Carbon monoxide was found as an intermediate product of the oxidation process. The presence of ceria in the catalyst has a strong effect on acetylene oxidation, which was found to be a direct bifunctional reaction between acetylene adsorbed on the noble metal and oxygen from ceria.

A transient kinetic model for the partial oxidation of acetylene to carbon monoxide was constructed on the basis of the experimental results and literature data. This model was combined with the same model for the transient carbon monoxide oxidation as used in the steady state study. This combined model is able to describe quantitatively the transient oxidation of acetylene as well as the simultaneous acetylene and carbon monoxide oxidation. An assumption for a selective deactivation through deposition of carbonaceous deposits of the catalyst had to be made, in order to describe both CO$_2$ peaks adequately. It was concluded that the presence of gaseous carbon monoxide hardly influences the oxidation of acetylene. On the other hand, the oxidation of carbon monoxide is almost completely inhibited by acetylene, except for the path leading to OCO species on the surface. Furthermore, carbon monoxide and acetylene are both oxidised, by oxygen adatoms from the previous half-cycle, in the same reaction front, which moves through the reactor after the switch from lean to rich conditions. Before this front, the oxidation reactions proceed with oxygen from ceria.

Although steady state and transient kinetics are completely different, both models are compatible regarding the reaction steps, the latter giving more detailed information. The rate parameters for transient and steady state kinetics are not identical.

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KINETICS OF NITRIC OXIDE REDUCTION BY CARBON MONOXIDE


**Abstract**

The reduction of NO by CO in absence and presence of O\(_2\) has been investigated by transient experiments at automotive cold-start conditions over commercial Pt/Rh/CeO\(_2\)/\(\gamma\)-Al\(_2\)O\(_3\), and derived model catalysts. A high resolution magnetic sector mass spectrometer was used for distinguishing between CO and N\(_2\) and between CO\(_2\) and N\(_2\)O. Mechanisms are compared for the different catalyst formulations. A kinetic scheme of elementary reaction steps is proposed, which highlights the various contributions of the catalyst constituents. The kinetic rate coefficients have been determined via regression of the transient experiments. The kinetic model quantifies storage and release of O\(_2\) and NO in ceria during lean and rich half-cycles.

**5.1. Introduction**

The NO reduction to N\(_2\) has proven to be a large problem, because of a low conversion of NO in the exhaust gas under lean conditions. This is also a main drawback of the application of lean-burn and diesel engines, which produce exhaust gases with high oxygen concentrations. The mechanism of the catalytic reduction of NO for automotive purposes has been widely studied. Notably NO reduction by hydrocarbons draws a lot of attention nowadays for its potential application under net oxidising conditions. NO reduction by CO under excess oxygen, however, is still not very well understood from a viewpoint of elementary step kinetics, which is an important item since automotive operating conditions are dynamic while ceria is present in automotive catalysts as an oxygen storage component. Therefore, the NO reduction by CO is studied in this chapter with transient kinetic methods via cycling of the reactor feed composition.

As noble metals Pt, Rh, Ru, Pd, Ir and alloys on alumina, ceria and ceria/alumina have been investigated (Muraki & Fujitani, 1986). Rh containing catalysts were found to achieve higher NO conversion than other noble metals (Matyshak et al., 1988; Granger et al., 1998b).
The type of support material was found to have a small influence on the kinetics of the NO reduction (Oh & Eickel, 1991). An exception concerns the presence of ceria. Ceria can take up the oxygen from dissociating NO on the noble metal (Oh & Eickel, 1991; Underwood & Bell, 1988), although this is also explained by an oxygen spill-over from the noble metal to the ceria surface (Lööf et al., 1991). Furthermore, it was found that NO is able to adsorb onto reduced ceria in combination with oxygen transfer from ceria to the noble metal (Cordatos & Gorte, 1996; Trovarelli et al., 1999; Diwell et al., 1990). Maunula et al. (1997) investigated the reduction of NO by hydrogen over several catalysts with transient response techniques. They found that ceria containing catalysts have a higher activity and a higher surface capacity than catalysts without ceria. Trovarelli et al. (1999) mention that NO adsorbs onto ceria which promotes NO desorption as $N_2$ at much lower temperatures than ceria free samples.

Generally, three different mechanisms have been proposed in literature. The most used mechanism (Granger et al., 1998a; Sadhankar & Lynch, 1997; Fink et al., 1991; Lorimer & Bell, 1979; Hecker & Bell, 1983, Pernama et al., 1997) involves reversible associative adsorption of both CO and NO on vacant noble metal sites. Subsequent NO dissociation requires another vacant noble metal site. The nitrogen adatoms may recombine to form $N_2$, or react with another adsorbed NO to form either gaseous $N_2O$ or gaseous $N_2$, leaving an oxygen adatom on the surface. Adsorbed CO reacts with oxygen adatoms to give gaseous $CO_2$. According to Pernama et al. (1997), this mechanism is not altered when oxygen is present in the gas phase. Leclerq et al. (1991) proposed a similar mechanism to explain the reduction of NO by CO in the presence of $O_2$. Generally it is concluded that $O_2$ adsorption inhibits the NO reduction, but at very low oxygen concentrations oxygen may create additional vacant sites, leading to an enhancement of the NO dissociation.

In an alternative mechanism (Klein et al., 1985; Banse et al., 1989; Huinink, 1995), the dissociation of adsorbed NO does not require a vacant noble metal site, but is assisted by adsorbed CO, yielding gaseous $CO_2$, a nitrogen adatom and a vacant site. The influence of oxygen was not considered in that context.

Another mechanism (Kudo et al., 1990; Carballo et al., 1989; Cho, 1989) proposes two adsorbed NO molecules, which react together to form either gaseous nitrogen or $N_2O$ and oxygen adatoms. Also in this case, no vacant sites for NO dissociation are required and this mechanism is said not to be altered by the presence of gaseous oxygen (Carballo et al., 1989). Not many kinetic modelling studies of NO reduction by CO in the presence of $O_2$ have been reported. Carballo et al. (1989) measured reaction rates under vacuum over Pt, Rh, and Pd catalysts and propose a mechanism. No rate constants are reported however. Steady state modelling of the NO-CO reaction without $O_2$ has been performed by several researchers over several catalysts: Oh (1990) Rh/Al$_2$O$_3$+CeO$_2$, Granger et al. (1998a,b) Pt/Rh/Al$_2$O$_3$ and several Pt based catalysts, Sadhankar & Lynch (1997) Pt/Al$_2$O$_3$ and Klein et al. (1985) Pt. These authors use similar models as described above and report rate coefficients. The transient reduction of NO by CO (without $O_2$) has been reported by Cho et al. (1989) over Rh/CeO$_2$/Al$_2$O$_3$ and Sadhankar & Lynch (1996) over Pt/Al$_2$O$_3$. The latter do not report rate coefficients and the former only model the rate determining step. Banse et al. (1989) have performed transient experiments under vacuum over Pt. They also use a type of rate determining step modelling. In all modelling studies, the effect of ceria is not explicitly taken into account.

This chapter provides new mechanistic insight about the contributions of the separate components of a commercial Pt/Rh/CeO$_2$/γ-Al$_2$O$_3$ three-way catalyst in terms of elementary
steps, e.g. the interactions of NO with ceria. A unique perspective is given, by comparing transient experiments over the Pt/Rh/CeO$_2$/γ-Al$_2$O$_3$ catalyst with experiments using the model formulations Pt/γ-Al$_2$O$_3$ and Pt/Rh/γ-Al$_2$O$_3$, and their respective carriers γ-Al$_2$O$_3$ and CeO$_2$/γ-Al$_2$O$_3$. The introduction of a high resolution mass spectrometer in this type of research allows measuring separately all relevant compounds, including CO and N$_2$, as well as CO$_2$ and N$_2$O. Furthermore, this chapter provides kinetic rate coefficients of the transient elementary step model for NO reduction by CO in the absence and presence of O$_2$ over the commercial three-way catalyst. The model is able to adequately predict NO reduction experiments at cold-start temperatures under both rich and lean conditions. Storage effects of ceria and noble metal-ceria interactions are explicitly taken into account. Furthermore, the model predicts surface coverages on the various active locations of the catalyst.

5.2. Experimental

The catalysts used in this study are Pt/γ-Al$_2$O$_3$, Pt/Rh/γ-Al$_2$O$_3$ and Pt/Rh/CeO$_2$/γ-Al$_2$O$_3$ as well as the separate carriers γ-Al$_2$O$_3$ and CeO$_2$/γ-Al$_2$O$_3$. All mentioned catalysts and carriers have been pre-treated according to the procedure described in Chapter 2. All catalysts contain 0.4 weight % Pt and (if applicable) 0.08 weight % Rh. The dispersion of the catalysts are not equal, because of the different noble metals and carriers. Details about these catalysts and carriers can be found in Campman (1996). Compared to chapters 3 and 4, the gas analysis was changed. The transients in the gas composition were monitored in real time just above and below the catalyst bed by an on-line magnetic sector mass spectrometer (Jeol JMS-GCmate) at a resolution of 5000 (20% cut), enabling separation of the isobaric masses of CO (m/e = 27.9949) and N$_2$ (m/e = 28.0062) on the one hand, and CO$_2$ (m/e = 43.9898) and N$_2$O (m/e = 44.0011) on the other hand. Mass spectrometry analysis was carried out in Selected Ion Monitoring (SIM) mode with a sampling frequency of 25 Hz on N$_2$, CO, NO, O$_2$, CO$_2$, N$_2$O, and NO$_2$. More details can be found in chapter 2. An example of measured inlet signals of CO, NO, and O$_2$ versus time can be seen in figure 5.1. The range of the experimental conditions is depicted in table 5.1.

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</tr>
<tr>
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<td>kPa</td>
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<td>K</td>
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</table>

**Figure 5.1.** Reactor inlet concentrations versus time, alternating 0.5 vol.% CO in He with 0.1 vol.% NO and 0.4 vol.% O$_2$ in He at 1/10 Hz.
5.3. Experimental results and discussion

In this section, the experimental results are presented and discussed in order of increasing catalyst complexity. First, the influence of the separate carriers is shown, and afterwards an elementary step model for Pt/γ-Al₂O₃ is discussed, based on the experimental results. Subsequently, the differences between this catalyst and the Pt/Rh/γ-Al₂O₃ and Pt/Rh/CeO₂/γ-Al₂O₃ catalysts are presented. All experiments shown were performed at a reactor temperature of 548 K. The oxidation of carbon monoxide is assumed to proceed as described by the kinetic models of Nibbelke et al. (1998) for the ceria containing Pt/Rh/CeO₂/γ-Al₂O₃ catalyst and Hoebink et al. (1999) for the Pt/γ-Al₂O₃ catalyst. The reaction steps of the transient model for CO oxidation by Nibbelke et al. are shown in table 5.2, as steps 1 to 10.

5.3.1. The carriers: \(\gamma\)-Al₂O₃ and CeO₂/\(\gamma\)-Al₂O₃

No reaction or adsorption of NO, CO, and O₂ on the support \(\gamma\)-Al₂O₃ was observed. The carrier can therefore be assumed as inert. In a previous study, it was found that CO₂ can reversibly adsorb onto the carrier (Hoebink et al., 1999; Nibbelke et al., 1998).

The ceria/alumina carrier, containing 28 wt. % ceria, was investigated for its behaviour towards NO. Starting from completely reduced ceria, it was found that NO is able to adsorb on and desorb from the ceria surface. Figure 5.2 shows reactor outlet concentrations of NO versus time when 0.1 vol. % NO in He is alternated with pure He at 1/20 Hz. The delay in reaching the 0.1% inlet level (interval = 20-30 s) corresponds with NO adsorption, while the tail approaching zero (t = 30-40 s) concerns NO desorption. When adsorption on ceria sites is assumed, it can be described as:

\[
\text{NO}_{(s)} + s \leftrightarrow \text{NO}_s
\]

In this text, the forward step will be referred to as step \#f, while the backward step is alluded to as step \#b. Here "s" denotes vacant sites on ceria. A subsequent experiment with NO and CO in alternating feeds did not yield significantly reaction products, thus excluding chemical reactions on the surface. Apparently ceria is unable to dissociate NO at 548 K. Also, no significant adsorption and desorption of CO was observed.

When oxygen is fed to ceria after the standard pre-treatment procedure (Chapter 2) and exposure to NO, oxygen does not adsorb, meaning that NO blocks reduced ceria sites. Furthermore, after hours of exposure of ceria to NO, a very slow desorption of the latter into a helium flow can be observed even after hours of time-on-stream. This indicates that NO can...
diffuse into the reduced ceria lattice, as is already known for oxygen. As this process takes place on a time scale, much longer than the time scale of feed alterations during the transient experiments, NO bulk diffusion was discarded with respect to this type of experiments.

After reducing the ceria again for three hours with 5% H2 in He at 773K, the oxygen ability to adsorb onto ceria returned. When CO is fed to oxidised ceria, small amounts of CO2 are found. Significant CO conversion could however not be detected.

When, after long-time exposure to oxygen, NO and He are alternated again over the catalyst carrier, exactly the same adsorption and desorption behaviour is found as for the reduced ceria, see figure 5.2. This means that NO adsorbs on both reduced and oxidised ceria with the same rate. This requires additional elementary steps:

\[
\text{NO}_{(g)} + \text{Os} \leftrightarrow \text{NO}_{2}\text{s} \tag{12}
\]

Since, independent of the oxidation state of the ceria, the same amount of NO adsorbs or desorbs, it seems reasonable to assume that the same locations on the catalyst surface are involved. As no gaseous NO2 was observed during the experiment, it cannot be said whether actually NO2 is formed on the ceria, or both NO and O are co-adsorbed on the same site.

5.3.2. The Pt/\(\gamma\)-Al2O3 catalyst

Figure 5.3 shows the results of an experiment where 0.5 vol. % CO at the reactor inlet was alternated with 0.1 vol. % NO with a frequency of 1/10 Hz. At the end of the CO half-cycle (t = 1.0 s) the noble metal surface is assumed to be fully covered by CO. Immediately after the switch to the NO feed has been made, N2O, CO2, and N2 are detected at the end of the reactor. NO remains fully adsorbed by the reactor for approximately 0.3 s. At this temperature CO slowly desorbs, leaving vacant sites onto which NO can adsorb:

\[
\text{NO}_{(g)} + \text{*} \leftrightarrow \text{NO}^* \tag{13}
\]

Vacant sites on the noble metal are here written as "\(*". The production of N2O requires the dissociation of NO, which involves extra vacant sites:

\[
\text{NO}^{***} \rightarrow \text{N}^{**} + \text{O}^* \tag{14}
\]

N2O is then formed by:

\[
\text{NO}^{*} + \text{N}^* \leftrightarrow \text{N}_2\text{O}^{**} + \text{*} \tag{15}
\]

and subsequent desorption:

\[
\text{N}_2\text{O}^{*} \leftrightarrow \text{N}_2\text{O}_{(g)} + \text{*} \tag{16}
\]

Actually, the sorption of N2O is reversible, as will be shown later. The oxygen adatoms from the dissociating NO will be rapidly converted to CO2, which was believed to desorb instantaneously (Nibbelke et al., 1998).

The immediate formation of N2O together with CO2 indicates that both N2O formation (step 15) and desorption (step 16f) are fast under the conditions at that specific time. Nitrogen can be produced in two different ways, where the first is known to be more important at low temperatures (Sadhankar & Lynch, 1997; Carballo et al., 1989):

\[
\text{N}_2\text{O}^{*} \rightarrow \text{N}_{2(g)} + \text{O}^* \tag{17}
\]

\[
\text{N}^{**} + \text{N}^* \rightarrow \text{N}_2 + 2\text{*} \tag{18}
\]

As the N* coverage will be very low immediately after switching, and because N2O is formed immediately, step 17 is more likely to be of importance than step 18 right after the switch.

Finally, a small amount of NO2 is observed which gradually increases in time during the NO half cycle. The formation of NO2 requires oxygen adatoms, which will not be present in large
quantities just after the switch, but will accumulate on the catalyst surface when the NO half cycle proceeds. In a separate experiment it was found that NO is able to adsorb immediately on a Pt/γ-Al₂O₃ surface fully covered with oxygen, which justifies the forward step (the backward step will be discussed later):

\[ \text{NO}^{(g)} + \text{O}^* \leftrightarrow \text{NO}_2^* \]  
(19)

\[ \text{NO}_2^* \leftrightarrow \text{NO}_{2(g)}^* + ^* \]  
(20)

The data do not provide evidence for NO₂ adsorption as its concentration was quite low in all considered experiments, but it is logical to assume that NO₂ can adsorb on the noble metal (Fridel et al., 1998).

After the switch to the lean feed, adsorbed CO on the noble metal surface is gradually exhausted, and replaced by oxygen adatoms and N-containing species. This will lead to a decreasing number of vacant sites, slowing down especially the dissociation of NO (step 14) and the adsorption of NO (step 13f). Therefore, all reactions will gradually stop and the NO concentration will reach its inlet level.

Immediately after the switch from the NO feed to the CO feed is made, strong desorption of NO from the noble metal surface takes place, even to such an extent that the NO concentration temporarily exceeds its inlet level. Such phenomena have been seen before for Ru/SiO₂ and for Pt at 300 K (Brown & Gonzales, 1977; Comrie & Lambert, 1974). Apparently, NO desorption is a very fast process, which can occur via steps 13b and 19b. Re-adsorption of NO will then be prevented because of the faster adsorption of gaseous CO, which could be seen as a type of cross desorption. A role of adsorbed NO₂ in this process cannot be excluded, as will become clear later. Simultaneously, N₂O, N₂ and CO₂ are produced. This indicates that vacant sites arise on the noble metal surface, enabling dissociation of NO, leading to the mentioned products as described before. The CO₂ production could be ascribed to reaction between adsorbed CO and oxygen adatoms, or between gaseous CO and oxygen adatoms (Hoebink et al., 1999). A very low coverage of oxygen adatoms leads to a very low amount of gaseous NO₂.

Figure 5.4 shows the results of an experiment, similar to the one in figure 5.3, except for the fact that N₂O has been fed in the lean half cycle, instead of NO. It can be seen that adsorption of N₂O is (step 16b) a slower process than the adsorption of NO (step 13f), as the former adsorbs only in part on the noble metal surface immediately after the switch from CO to N₂O (t = 0 s). The N₂O adsorption is accompanied by N₂ production, which points to step 17.

After the initial break-through of the N₂O signal, N₂O adsorbs almost completely, when sufficient sites have become available through CO desorption and reaction to N₂ (step 17). The latter reaction yields oxygen adatoms, which will react with adsorbed CO. The slow start of the CO₂ production is remarkable, as O adatoms should be available from N₂O decomposition. It is possible that some N₂O decomposes into NO (step 15b), which can desorb (step 13b) and then cover the oxygen adatoms (step 19f).

When comparing figures 5.3 and 5.4, it can be seen that the reduction of N₂O (figure 5.4) yields much more N₂ than the reduction of NO (figure 5.3). There are two reasons: 1) the stoichiometry leads to twice as much N₂ in the case of N₂O compared to the reduction of NO, and 2) NO reduction requires vacant sites for the dissociation of NO (step 4), while vacant sites are not required for N₂O decomposition (step 17). This means that in the N₂O case the reactions will stop only when the surface becomes largely occupied with oxygen adatoms.
The latter apparently occurs near the end of the lean half-cycle, when \( \text{N}_2 \) and \( \text{CO}_2 \) production declines, and the \( \text{N}_2\text{O} \) concentration rises to the inlet level. A small amount of NO is observed as well, indicating that step 15 is reversible. The high O coverage is also resembled by the larger \( \text{CO}_2 \) peak, when switching from the \( \text{N}_2\text{O} \) half cycle to the \( \text{CO} \) half cycle (\( t = 5.3 \) s). It is remarkable that in the \( \text{N}_2\text{O} \) experiments similar quantities of \( \text{NO}_2 \) were measured as in the NO experiments. This also indicates that some \( \text{N}_2\text{O} \) decomposes into NO, which may adsorb on O adatoms and desorb as \( \text{NO}_2 \).

The outlet concentrations versus time of an experiment where \( \text{NO} + \text{O}_2 \) is alternated with CO can be seen in figure 5.5. When compared with the same experiment in the absence of oxygen (figure 5.3), the NO signal shows two major differences: much less adsorption takes place at the beginning of the NO half cycle showing even a small break through peak, and the desorption behaviour after the switch to the \( \text{CO} \) half cycle is completely different. The difference in adsorption can be explained by the relatively fast adsorption and reaction of oxygen. The \( \text{CO}_2 \) peak, when \( \text{O}_2 \) is fed, is high and sharp indicating a very fast oxidation of adsorbed \( \text{CO} \) by adsorbing \( \text{O}_2 \). This means that the surface will quickly be dominated by oxygen adatoms onto which NO is apparently able to adsorb quite slowly through step 19f. NO adsorbs immediately on both vacant sites (only few are available as can be seen from the small \( \text{N}_2 \) and \( \text{N}_2\text{O} \) production) and O adatoms, but both rates are too slow to reach a full NO conversion. NO adsorption on \( \text{O}^\ast \) leads to \( \text{NO}_2 \) desorption, as seen from the \( \text{NO}_2 \) gas phase concentration, which very slowly increases in time. The NO adsorption proceeds quite long, however, because the NO signal very slowly approaches its inlet level. \( \text{NO}_2 \) (step 20f) and NO (step 19b) desorption seems rather slow as appears from the tailing of the \( \text{NO}_2 \), NO, and \( \text{CO}_2 \) signals.

After the switch to the \( \text{CO} \) half cycle, oxygen adatoms are available for reaction with \( \text{CO} \) to \( \text{CO}_2 \) either directly or by desorption of NO from adsorbed \( \text{NO}_2 \). The relatively large \( \text{NO}_2 \) peak (\( t = 6.5 \) s) indicates vacant sites become available as well. The catalyst surface is mostly covered with \( \text{NO}_2 \) at the end of the lean half-cycle. This is supported by the long tail in the \( \text{CO}_2 \) signal, which emanates from the oxygen adatoms formed by a slow \( \text{NO}_2 \) decomposition. The high and immediate peak in the \( \text{CO}_2 \) signal may indicate that \( \text{CO} \) reacts via both Langmuir-Hinselwood and Eley-Rideal type of steps (Hoebink et al., 1999). At both switching moments, the production of \( \text{N}_2 \) and \( \text{N}_2\text{O} \) is very low, because of the low fraction of vacant sites on the noble metal, which are required for the dissociation of NO (step 14). The \( \text{NO}_2 \) responses at the second half of both half cycles follow the gas phase concentration of NO in either a slow decrease (\( \text{CO} \) half cycle) or a slow increase (NO half cycle).

5.3.3. The Pt/Rh/\( \gamma \)-Al\(_2\)O\(_3\) catalyst

The influence of Rh in the catalyst is derived from a comparison of transient experiments on a Pt/Rh/\( \gamma \)-Al\(_2\)O\(_3\) catalyst and on the Pt/\( \gamma \)-Al\(_2\)O\(_3\) catalyst, described before. Figure 5.6 shows an experiment with alternating 0.5 vol. % \( \text{CO} \) in He and 0.1 vol. % \( \text{NO} \) in He. This figure compares with figure 5.3 on the Pt catalyst. The major difference is the larger conversion of all compounds on the Pt/Rh catalyst. The \( \text{CO}_2 \) peak at the switch from the \( \text{CO} \) feed to the NO feed (\( t = 1.3 \) s) has a much larger area. This area is almost fully determined by the amount of \( \text{CO} \) adsorbed on the catalyst just before this switch. The larger area indicates that the Pt/Rh catalyst simply contains more active noble metal sites than the Pt catalyst. This already explains the major differences between the two catalysts. There are however some other dissimilarities.
Immediately after the switch from the CO feed to the NO feed \((t = 1.3 \text{ s})\) more \(N_2\) and less gaseous \(N_2O\) is produced than on the Pt catalyst, which indicates that the decomposition of \(N_2O\) is faster on the Pt/Rh catalyst. The enhanced dissociation of NO, caused by the presence of Rh, can also be seen from the quite large \(N_2\) peak at the switch from NO to CO \((t = 6.0 \text{ s})\). The NO signal misses its sharp desorption peak, which is present in the Pt catalyst experiment. Clearly, the dissociation/desorption ratio of NO is more favourable when Rh is present.

While the Pt catalyst produces \(N_2O\) two times per period, the \(N_2O\) signal from the Pt/Rh catalyst has three maxima. At the end of the CO half cycle, the noble metal surface is more or less fully covered with CO. After the switch to NO has been made, some CO will desorb, and NO can adsorb (step 13) and partly dissociate (step 14) on the vacant sites. This will give \(N^*\) next to \(NO^*\) on the noble metal surface leading to the first \(N_2O\) maximum at \(t = 1.3 \text{ s}\) (steps 15 and 16). The proceeding reactions produce extra vacant sites, which enhances the dissociation rate of NO, and decreases the \(N_2O\) production. When surface CO gets depleted, \(CO_2\) formation decreases, so it will become more difficult to remove \(O^*\) from the surface. Due to fewer vacant sites, not all NO can dissociate anymore, and the resulting N adatoms next to molecular adsorbed NO will form \(N_2O\) for the second time in the NO half cycle. This does not last long, however, because the vacant sites on the noble metal surface will be rapidly filled with \(NO^*\) and \(O^*\) preventing further reactions until the end of the lean half-cycle. Only when the switch to the CO feed is made \((t = 6 \text{ s})\), again some vacant sites are created to invoke \(N_2O\) production.

Also for the Pt/Rh catalyst the influence of the presence of oxygen is large. Figure 5.7 shows the results of a transient experiment where CO is alternated with a mixture of NO and \(O_2\). This figure is compared to figure 5.5 for the Pt catalyst. Especially the conversion of CO and \(O_2\) is much higher over the Pt/Rh catalyst, resulting in larger \(CO_2\) peaks. Also more NO is converted to \(N_2\) as was also seen in the experiments without \(O_2\). NO adsorption is more pronounced and there is less desorption. These aspects can again be ascribed to the above mentioned changes in number of sites, leading to higher conversions of all compounds. Also reaction rates for most steps involving NO will be higher on the Pt/Rh catalyst compared to the Pt catalyst. Summarising the effect of Rh addition to a Pt catalyst, it can be said that the mechanism is not altered, but that the rates of especially the following steps are higher: NO dissociation (step 13), \(N_2O\) decomposition (step 17), \(NO_2\) formation (step 19f). This is an important conclusion for kinetic modelling, as it appears that no distinction has to be made between Pt and Rh sites.

5.3.4. The Pt/Rh/\(CeO_2/\gamma-Al_2O_3\) catalyst

The experimental results from the previous section are compared with similar transient experiments over a commercially available Pt/Rh/\(CeO_2/\gamma-Al_2O_3\) catalyst. As this catalyst contains ceria, steps 11 and 12 apply here as well. Figure 5.8 shows the results of an NO reduction experiment in the absence of \(O_2\), which is comparable with the experiment from figure 5.6 over the Pt/Rh catalyst. The major differences between the two experiments are the amounts of \(N_2\) and \(CO_2\) produced: the ceria containing catalyst produces more than twice as much of both products. As was mentioned before, the production of \(N_2\) during the NO half cycle will stop when NO dissociation is hindered by absence of vacant sites because of accumulation of oxygen adatoms on the noble metal surface. The fact that this moment is strongly delayed for the ceria catalyst, indicates that ceria is able to take oxygen from
Figure 5.3. Reactor outlet concentrations versus time, alternating 0.5 vol.% CO in He with 0.1 vol.% NO in He at 1/10 Hz. at 548 K over Pt/γ-Al₂O₃.

Figure 5.4. Reactor outlet concentrations versus time, alternating 0.5 vol.% CO in He with 0.1 vol.% N₂O in He at 1/10 Hz. at 548 K over Pt/γ-Al₂O₃.

Figure 5.5. Reactor outlet concentrations versus time, alternating 0.5 vol.% CO in He with 0.1 vol.% NO and 0.4 vol.% O₂ in He at 1/10 Hz. at 548 K over Pt/γ-Al₂O₃.

Figure 5.6. Reactor outlet concentrations versus time, alternating 0.5 vol.% CO in He with 0.1 vol.% NO in He at 1/10 Hz. at 548 K over Pt/Rh/γ-Al₂O₃.
Figure 5.7. reactor outlet concentrations versus time, alternating 0.5 vol.% CO in He with 0.1 vol.% NO and 0.4 vol.% O$_2$ in He at 1/10 Hz. at 548 K over Pt/Rh/γ-Al$_2$O$_3$.

Figure 5.8. reactor outlet concentrations versus time, alternating 0.5 vol.% CO in He with 0.1 vol.% NO in He at 1/10 Hz. at 548 K over Pt/Rh/CeO$_2$/γ-Al$_2$O$_3$.

Figure 5.9. reactor outlet concentrations versus time, alternating 0.5 vol.% CO in He with 0.1 vol.% NO and 0.4 vol.% O$_2$ in He at 1/10 Hz. at 548 K over Pt/Rh/CeO$_2$/γ-Al$_2$O$_3$. 
dissociated NO. Two possible pathways for this process are known from literature: oxygen adatoms could spill over to the ceria surface (Lööf et al., 1991), or a type of bifunctional dissociation of NO adsorbed on the noble metal could take place (Oh & Eickel, 1991; Underwood & Bell, 1988):

$$\text{NO}^* + s \rightarrow \text{N}^* + \text{Os}$$  \hspace{1cm} (21)

As can be seen in figure 5.8 (t = 2-6 s), the NO conversion is complete for almost the entire half cycle, and also the N₂O production is very low. Under these conditions the dissociation of NO is quite fast, so the fractional surface coverage of NO is expected to be very low. The main path for N₂ formation is therefore likely to be the recombination of two N adatoms into N₂ (step 18). Only near the end of the NO half cycle, the N₂O and NO concentrations start to rise, indicating a significant decrease in the fraction of vacant sites. The absence of a large amount of oxygen on the noble metal also leads to a very low amount of NO₂ produced. The increased oxygen storage can very well be seen from the large CO₂ peak after the switch from the NO to the CO half cycle. Its increased area, compared with the experiment over the Pt/Rh catalyst, is directly related with the larger oxygen storage capacity of the ceria catalyst. Besides the presence of ceria, also a larger noble metal dispersion is a partial explanation for larger storage capacities of the catalyst.

As hardly any NO is present on the catalyst, no desorption is detected after the switch to the CO feed. It is remarkable that the amount of CO₂ produced in the NO half cycle over the ceria containing catalyst is more than the corresponding amount of CO₂ produced in the NO half cycle over the Pt/Rh catalyst. Principally, the amount of CO₂ produced after the switch to the NO feed, is solely determined by the amount of CO on the catalyst just before the switch is made. Apparently, the ceria containing catalyst can store more CO than the Pt/Rh catalyst. The higher noble metal capacity can probably only partly explain this difference. Other explanations could be reversible CO spill over from the noble metal to the ceria, or differences in CO adsorption/desorption equilibria leading to higher surface coverages on the ceria catalyst compared to the Pt/Rh catalyst during the rich half cycle.

The transient reduction of NO by CO in the presence of O₂ over the commercial Pt/Rh/CoO₂/γ-Al₂O₃ catalyst can be seen in figure 5.9. Compared with figure 5.7 for the Pt/Rh catalyst, it can be seen that ceria has a large influence on all conversions. When ceria is present much more NO adsorbs, but significantly less than in the absence of oxygen (figure 5.8). Combined with the fact that much less N₂ is produced, it can be concluded again that the dissociation of NO is largely inhibited by the oxygen on the noble metal. Oxygen inhibition does not hinder NO adsorption on ceria, which NO is released after the switch to the CO feed is made. The desorption peak is likely a combination of desorption from the noble metal, probably from NO₂* decomposition because of the relatively slow desorption, and desorption of NO from ceria. The N₂O signals follow the N₂ signals, indicating that under these conditions the decomposition of N₂O is the most important path for N₂ formation.

Both CO₂ peaks are larger for the commercial catalyst than for the Pt/Rh catalyst. As before, the CO₂ peak in the CO half cycle can be explained by the presence of oxygen on ceria, which can oxidise CO on the noble metal via the bifunctional path (Nibbelke et al., 1998). This path is hindered by NO, adsorbed onto ceria oxygen (step 12) explaining the long CO₂ tail at the last part of the half cycle. The increased CO₂ production after the switch to the NO+O₂ half cycle can again only be explained by the presence of CO on the ceria caused by reversible spill over from the noble metal during the CO half cycle:
CO* + s ↔ * + CoS

A complete model for NO reduction by CO under net oxidising conditions over Pt/Rh/CeO$_2$/γ-Al$_2$O$_3$ catalyst is summarised in Table 5.2, which results from adding additional steps for bifunctional reactions and reactions on ceria to the elementary step model, proposed for the noble metal catalyst without ceria.

<table>
<thead>
<tr>
<th>No.</th>
<th>Elementary reaction step</th>
<th>Coefficient</th>
<th>No.</th>
<th>Elementary reaction step</th>
<th>Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CO$_{(g)}$ + * ↔ CO *</td>
<td>$k_{1}^{f}, k_{1}^{b}$</td>
<td>6</td>
<td>OCO* ↔ CO$_2$ + *</td>
<td>$k_{6}^{f}$</td>
</tr>
<tr>
<td>2</td>
<td>O$_{(g)}$ + * ↔ O2 *</td>
<td>$k_{2}^{f}$</td>
<td>7</td>
<td>O$_2$ + s → O$_2$s</td>
<td>$k_{7}^{f}$</td>
</tr>
<tr>
<td>3</td>
<td>O$_2$ + * ↔ 2O *</td>
<td>$k_{7}^{f}$ (∞)</td>
<td>8</td>
<td>O$_2$s + s → 2Os</td>
<td>$k_{8}^{f}$ (∞)</td>
</tr>
<tr>
<td>4</td>
<td>CO* + Os → CO$_2$ + 2 *</td>
<td>$k_{4}^{f}$</td>
<td>9</td>
<td>CO* + Os → CO$_2$(g) + * + s</td>
<td>$k_{9}^{f}$</td>
</tr>
<tr>
<td>5</td>
<td>CO$_{(g)}$ + O* ↔ OCO *</td>
<td>$k_{5}^{f}, k_{5}^{b}$</td>
<td>10</td>
<td>CO$_2$(g) + γ → CO$_2$γ</td>
<td>$k_{10}^{f}, k_{10}^{b}$</td>
</tr>
<tr>
<td>11</td>
<td>NO$_{(g)}$ + s ↔ NOs</td>
<td>$k_{11}^{f}, k_{11}^{b}$</td>
<td>20</td>
<td>NO$_2$ + s ↔ NO$_2$(g) + *</td>
<td>$k_{20}^{f}, k_{20}^{b}$</td>
</tr>
<tr>
<td>12</td>
<td>NO$_{(g)}$ + Os ↔ NO$_2$s</td>
<td>$k_{12}^{f}, k_{12}^{b}$</td>
<td>21</td>
<td>NO * + s → N * + Os</td>
<td>$k_{21}^{f}$</td>
</tr>
<tr>
<td>13</td>
<td>NO$_{(g)}$ + + ↔ NO *</td>
<td>$k_{13}^{f}, k_{13}^{b}$</td>
<td>22</td>
<td>CO + * + s ↔ + + CoS</td>
<td>$k_{22}^{f}, k_{22}^{b}$</td>
</tr>
<tr>
<td>14</td>
<td>NO * + + + ↔ N * + O *</td>
<td>$k_{14}^{f}$</td>
<td>23</td>
<td>O * + CoS → CO$_2$(g) + * + s</td>
<td>$k_{23}^{f}$</td>
</tr>
<tr>
<td>15</td>
<td>NO * + N * ↔ N$_2$O * + *</td>
<td>$k_{15}^{f}$ (k$_{15}^{b}$)</td>
<td>24</td>
<td>O$_2$s + m ↔ s + O$_2$m</td>
<td>$k_{24}^{f}, k_{24}^{b}$</td>
</tr>
<tr>
<td>16</td>
<td>N$_2$O* ↔ N$_2$O$_2$(g) + *</td>
<td>$k_{16}^{f}$ (k$_{16}^{b}$)</td>
<td>25</td>
<td>NO$_2$s + Os ↔ Os + NO$_2$m</td>
<td>$k_{25}^{f}, k_{25}^{b}$</td>
</tr>
<tr>
<td>17</td>
<td>N$_2$O* ↔ N$_2$(g) + O *</td>
<td>$k_{17}^{f}$</td>
<td>26</td>
<td>NO$_2$s + Os ↔ Os + NO$_2$m</td>
<td>$k_{26}^{f}, k_{26}^{b}$</td>
</tr>
<tr>
<td>18</td>
<td>N * + N * ↔ N$_2$(g) + 2 *</td>
<td>$k_{18}^{f}$</td>
<td>27</td>
<td>NO$_2$s + Os ↔ Os + NO$_2$m</td>
<td>$k_{27}^{f}, k_{27}^{b}$</td>
</tr>
<tr>
<td>19</td>
<td>NO$_{(g)}$ + O* ↔ NO$_2$ *</td>
<td>$k_{19}^{f}, k_{19}^{b}$</td>
<td>28</td>
<td>NO$_2$s + m ↔ Os + NO$_2$m</td>
<td>$k_{28}^{f}, k_{28}^{b}$</td>
</tr>
</tbody>
</table>

5.4. Kinetic modelling

The objective of the modelling work is to construct a transient kinetic model, which allows to give an adequate description of the measured N$_2$, CO, NO, O$_2$, CO$_2$, N$_2$O, and NO$_2$ concentrations at the reactor outlet with a given inlet in time.

5.4.1. Reaction kinetics

The chemical reaction steps used for kinetic modelling are shown in Table 5.2. A 's' denotes a site on the noble metal, where no distinction was made between Rh and Pt atoms. It is generally known that Rh addition to Pt catalysts enhances the reduction rate of NO to N$_2$, but it was found in section 5.3.3. that the influence of Rh could be included into the model by increasing the rate coefficients for certain steps. As the noble metal surface composition is unknown, and may change during the transients because of reduction and oxidation of the noble metal surface (van Delft et al., 1989; Wolf et al., 1989), an assumption of only one type of noble metal sites is the only realistic solution. This effect is expected to be the largest for the steps which are accelerated by the presence of Rh, as mentioned in section 5.3.3.

Steps 1-10 have directly been taken from Nibbelke et al. (1998). Steps 11-21 have been described in detail in section 5.3. During the modelling process, it became clear that some
model extensions had to be made. Oxidation of ceria CO by noble metal oxygen (step 23) had to be taken into account, as an addition to the reversible spill-over of CO from the noble metal (step 22). During the rich half-cycle, the ceria surface will be mainly vacant, allowing step 22f to proceed extensively. However, the noble metal surface will almost completely be filled during the entire period, making step 22b very slowly. Since the experiment shows that a large part of the extra CO (i.e. on the ceria surface) is oxidised, step 23 is introduced. A direct reaction between CO adsorbed on the ceria surface and oxygen adsorbed on the ceria surface could be excluded from the model, because it was experimentally found that a CeO2/γ-Al2O3 'catalyst' did not show any CO oxidation activity at the investigated range of conditions.

As mentioned in section 5.3.1. a strong indication was given that ceria is able to store large amounts of nitric oxide. The initial assumption that the time scale of transport of nitric oxide from the surface to the bulk is much larger than the time scale of the transient experiments did not appear to be completely valid. Therefore, it is considered that a ceria sub-layer is present, which can contain both oxygen and nitric oxide species. It is believed that, at the used temperatures, only a small layer of the bulk phase immediately below the ceria surface is involved in reactions at the considered time scale, and only as storage and release of nitric oxide and oxygen. This is represented by steps 24 to 28 in table 5.2. At relatively high temperatures (673 K), large heat effects were observed when switching from a rich to a lean feed, indicating the exothermic oxidation of ceria (step 24f, table 5.2). Also, because of the small distance between the ceria surface and the ceria sub-layer in combination with the effort to reduce calculation times as much as possible, a choice was made to describe transfer of oxygen and nitric oxide from the surface ceria to a subsurface ceria layer and the reverse rather as chemical reaction steps instead of diffusion processes. The capacity of the ceria subsurface layer increases with temperature, which is modelled with an Arrhenius equation. For the investigated temperature range, as well as lower temperature ranges, this will give an adequate description. For higher temperatures additional research will be needed to investigate the NOx storage capacity as a function of temperature. The reason that ceria is not an effective NOx storage catalyst for e.g. diesel exhaust treatment is the fact that the NOx is released from the ceria as soon as no more gaseous nitric oxide is present, whereas BaO for example will retain the NOx until rich conditions are met. The steps for the oxidation and reduction of the ceria sub-surface layer have been introduced in order to describe the observed slow oxidation at the end of the rich half-cycle. Since no difference was observed between nitric oxide adsorption and desorption between the reduced and oxidised ceria, the reaction steps have been introduced for both adsorbed NOs (steps 25 and 26) and adsorbed NO2s (steps 27 and 28), with the same rate coefficients (k25f and k25b).

For the modelling the rates of steps 15b and 16b (table 5.2) have been neglected. This was done because the surface coverage and gas phase concentration of N2O is expected to be very low under all used conditions.

5.4.2 Reactor model equations

The fixed-bed laboratory reactor is regarded as an ideal isothermal plug flow reactor. The reactor model consists of the continuity equations for (1) N2, CO, NO, O2, CO2, N2O and NO2 in the gas phase, (2) surface species adsorbed on the noble metal surface, (3a) surface species adsorbed on the ceria surface, (3b) species in the ceria sub-layer, (4) CO2 adsorbed on the γ-Al2O3 support:
The experimentally measured reactor inlet concentrations were used to produce model predictions for the concentration responses at the reactor outlet. The reactor inlet concentrations of $N_2$, $CO_2$, $N_2O$ and $NO_2$ were always kept zero.

The production rates of the different gaseous compounds are calculated from the rates of the elementary reaction steps in the reaction mechanism listed in table 5.2 which is considered in the previous section. The reaction rates of the elementary reaction steps are calculated via the law of mass action.

The model calculations and regression analysis have been performed in a similar way as in chapters 3 and 4. Estimation of the kinetic parameters was performed with non-linear multi-response regression analysis of the $N_2$, $CO$, $NO$, $O_2$, $CO_2$, $N_2O$, and $NO_2$ concentrations at the reactor outlet. The simultaneous regression was carried out for experiments at a frequency of $1/10$ Hz at temperatures of 523, 548, and 573 K. At first, all rate parameters of the $CO$ oxidation sub-model (393 - 433 K, (Nibbelke et al., 1998)) were fixed. Later, however, it appeared that extrapolation from 393 to 523 K of the rate coefficients for the Langmuir-Hinshelwood reaction between $CO^*$ and $O^*$ (step 4) and the desorption of $CO^*$ (step 1b) was not reliable; both values of the rate coefficients became unrealistically high at temperatures above 500 K. Therefore, these parameters were adapted in such a way, that they can be used in the entire temperature range from 393 to 573 K ($A_{1b}^b = 8.49 \times 10^{11} s^{-1}$, $E_{1b}^b = 87.9$ kJ/mol; $A_4 = 2.0 \times 10^7 s^{-1}$, $E_4 = 49.1$ kJ/mol). The capacity of the ceria sub-layer, which is introduced to account for ceria bulk oxygen and $NO$, was also determined by regression. The temperature dependence of this capacity is modelled through an Arrhenius type equation ($A_{CeB}$, $E_{CeB}$ in table 5.3).

### 5.4.3. Kinetic model equations

The fractions of vacant sites on the noble metal ($\theta_s$), on the ceria surface ($\xi_s$), and in the ceria sub-layer ($\xi_m$) are defined as:

\[
\begin{align*}
\theta_s &= 1 - \theta_O - \theta_{OCO} - \theta_{NO} - \theta_N - \theta_{N_2O} - \theta_{NO_2}, \\
\xi_s &= 1 - \xi_O - \xi_{NO} - \xi_{N_2O} - \xi_{CO}, \\
\xi_m &= 1 - \xi_O - \xi_{NO} - \xi_{NO_2}.
\end{align*}
\]

All fractions are defined as number of sites, relative to the total number of noble metal or ceria sites. The production rates for the gas phase components are straightforward (see Chapters 3 and 4). As an example the production rates for NO and CO are presented:

\[
\begin{align*}
\sum_k L_k R_{k,CO} &= L_{NM}(-k_{12}^f C_{CO} \theta_s + k_{13}^b \theta_{NO} - k_{19}^f \theta_O C_{CO} + k_{18}^b \theta_{OCO}) \\
\sum_k L_k R_{k,NO} &= L_{NM}(-k_{12}^f C_{NO} \theta_s + k_{13}^b \theta_{NO} - k_{19}^f \theta_O C_{NO} + k_{18}^b \theta_{NO_2}) - L_{CeS}(k_{12}^f C_{NO} (\xi_s + \xi_O) - k_{12}^b (\xi_{NO} + \xi_{NO_2}))
\end{align*}
\]
Also as examples, for insertion into the reactor model equations, production rates of NO on the noble metal surface and on the ceria surface as well as O in the ceria sub-layer are given:

\[
\sum_{k} L_{k} R_{k,NO} = L_{NM}(k_{11} C_{NO} \theta_{f} - k_{14} \theta_{NO} \theta_{f} - k_{15} \theta_{NO} \theta_{N} - k_{21} \theta_{NO} \xi_{f}) \\
\sum_{k} L_{k} R_{k,NO} = L_{CeS}(k_{11} C_{NO} \xi_{f} - k_{25} \xi_{NO} \xi_{f} - k_{25} \xi_{NO} \xi_{m} - k_{28} \xi_{NO} \xi_{O} - k_{26} \xi_{NO} \xi_{NO}) \\
\sum_{k} L_{k} R_{k,Om} = L_{CeB}(k_{24} \xi_{SO} \xi_{f} - k_{24} \xi_{SO} \xi_{O} - k_{26} \xi_{NO} \xi_{SO} + k_{26} \xi_{NO} \xi_{SO} - k_{27} \xi_{NO} \xi_{SO} + k_{27} \xi_{NO} \xi_{NO})
\]

Generally, adsorption steps were taken as temperature independent, whereas the rate parameters of surface reactions and desorption steps were described by Arrhenius equations. The kinetic rate parameters for CO oxidation (steps 1-10) and the catalyst properties were taken from (Nibbelke et al., 1998) with the minor adaptation for steps 1b and 4f as mentioned. The rate parameters, viz. activation energies and pre-exponential factors, for steps 11-28 were determined by non-linear regression. It was found that the rates for the NO reactions on ceria are independent of the oxidation state of ceria, so the rate parameters for the corresponding steps were taken as the same (i.e. steps 11 and 12 for oxygen, steps 25-28 for NO).

5.6. Modelling results

5.6.1. NO reduction by CO in the presence of oxygen

Figure 5.10 shows the measured and calculated reactor outlet concentrations for the experiment with oxygen at 523 K. Note that the N2, N2O, and NO2 concentrations are depicted on the right y-axis. Markers indicate measurements, drawn lines are model predictions.

<table>
<thead>
<tr>
<th>k11</th>
<th>6.46 \times 10^6</th>
<th>E16</th>
<th>45.3</th>
<th>A21^f</th>
<th>1.03 \times 10^4</th>
<th>E24^b</th>
<th>123</th>
<th>A11^b</th>
<th>5.56 \times 10^{11}</th>
</tr>
</thead>
<tbody>
<tr>
<td>E11^b</td>
<td>109</td>
<td>A17^f</td>
<td>4.64 \times 10^3</td>
<td>E21^f</td>
<td>168</td>
<td>A25^f</td>
<td>2.45 \times 10^5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>k13^f</td>
<td>3.63 \times 10^5</td>
<td>A18^f</td>
<td>4.08 \times 10^8</td>
<td>E22^f</td>
<td>185</td>
<td>A25^b</td>
<td>6.60 \times 10^6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E13^b</td>
<td>83.2</td>
<td>A19^b</td>
<td>5.85 \times 10^2</td>
<td>E22^b</td>
<td>51.1</td>
<td>A25^b</td>
<td>65.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A13^b</td>
<td>3.04 \times 10^{10}</td>
<td>A19^f</td>
<td>2.27 \times 10^3</td>
<td>A23^f</td>
<td>2.33 \times 10^4</td>
<td>L_{NM}</td>
<td>1.41 \times 10^2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E14^f</td>
<td>45.8</td>
<td>k19^f</td>
<td>5.85 \times 10^2</td>
<td>E23^f</td>
<td>46.0</td>
<td>L_{CeS}</td>
<td>6.59 \times 10^3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A14^f</td>
<td>2.19 \times 10^5</td>
<td>A20^f</td>
<td>2.18 \times 10^8</td>
<td>A24^f</td>
<td>1.71 \times 10^9</td>
<td>L_{CeB}</td>
<td>1.96</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E15^f</td>
<td>38.3</td>
<td>A20^b</td>
<td>97.8</td>
<td>E24^f</td>
<td>79.7</td>
<td>E_{CeB}</td>
<td>18.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>A15^f</td>
<td>2.71 \times 10^6</td>
<td>k20^b</td>
<td>5.34 \times 10^9</td>
<td>A24^b</td>
<td>6.08 \times 10^{12}</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In general the most important features of the experimental data is predicted by the model. Some minor deviations (i.e. the CO2 and CO signal, see figure 5.10) are probably due to the large temperature difference between the performed experiments and the extrapolated rate coefficients for CO oxidation, which were determined around 400 K. The N-containing gases have generally quite low concentrations. The large uptake and release of NO are predicted very well. Only the shape of the predicted NO2 signal is different from the measured one,
which could be caused by difficult MS calibration for NO₂. NO₂ cannot be fed directly to the
reactor using the experimental set-up, and most of the NO₂ (~ 96 %) dissociated upon
ionisation in the MS.

The rate coefficients obtained by this study are shown in table 5.3. As far as comparison is
possible, most of the presented rate coefficients have the same order of magnitude as similar
reaction steps found in literature. Granger et al. (1998a) studied steady state reaction kinetics
over several supported Pt catalysts and therefore only give lumped rate parameters, which can
only partially be compared with the values reported here. Furthermore, they found a strong
dependency of the support material on the rate coefficients. For CO and NO respective
equilibrium adsorption constants of 5.97 m³/mol and 0.705 m³/mol at 573 K are reported for
Pt/Al₂O₃. When recalculated, this works reports ratios of 109 and 459 respectively. The
differences can be due to the use of transient versus steady-state conditions, the use of a
different support and the presence of Rh in the present work. The value for the dissociation
rate parameter (3.167 × 10⁻⁶ mol/g/s) cannot be recalculated because the noble metal capacity is
not reported. The comparison between this work and the work by Oh et al. (1986) and
Sadhankar & Lynch can be seen in Table 5.4. Note that the catalysts used for the kinetic
studies contain different noble metals, and the catalysts from literature do not contain ceria.
This makes comparison more difficult.

### Table 5.4

Comparison of some of the rate parameters from literature sources with this work. Oh et al. (1986)
used a Rh/Al₂O₃ catalyst, Sadhankar & Lynch used a Pt/Al₂O₃ catalyst. ‘S’ represents a sticking coefficient for
the adsorption of NO. Dimensions: S: [-], A: s⁻¹, E: kJ/mol.

<table>
<thead>
<tr>
<th>no.</th>
<th>reaction step</th>
<th>Sadhankar &amp; Lynch, 1997</th>
<th>Oh et al., 1986</th>
<th>This work</th>
</tr>
</thead>
<tbody>
<tr>
<td>13f</td>
<td>NO + * → NO*</td>
<td>0.01 S⁻¹/A E</td>
<td>0.5 S⁻¹/A E</td>
<td>0.08 S⁻¹/A E</td>
</tr>
<tr>
<td>13b</td>
<td>NO* → NO + *</td>
<td>4.30 × 10⁸ 54.3</td>
<td>5.00 × 10¹³ 109</td>
<td>3.00 × 10¹⁰ 83.2</td>
</tr>
<tr>
<td>14f</td>
<td>NO* + * → N* + O*</td>
<td>1.60 × 10¹³ 116.8</td>
<td>6.00 × 10¹³ 80</td>
<td>2.20 × 10⁸ 45.8</td>
</tr>
<tr>
<td>18f</td>
<td>2N* → N₂ + 2*</td>
<td>3.00 × 10⁵ 79.1</td>
<td>3.00 × 10¹⁰ 31</td>
<td>4.10 × 10⁸ 56.6</td>
</tr>
<tr>
<td>15f</td>
<td>NO* + N* → N₂O</td>
<td>1.40 × 10⁹ 92.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>17f</td>
<td>N₂O* → N₂ + O*</td>
<td>2.50 × 10⁶ 72.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>16f</td>
<td>N₂O* + N* → N₂ + O*</td>
<td>-</td>
<td>2.00 × 10⁹ 88</td>
<td>-</td>
</tr>
<tr>
<td>18f</td>
<td>2N* + N₂O + *</td>
<td>2.20 × 10⁶ 45.8</td>
<td>4.60 × 10⁵ 20.1</td>
<td></td>
</tr>
</tbody>
</table>

As can be seen, the values for steps 13f and 13b are in between the literature values, which
could be expected because of the comparison between a Pt/Rh catalyst on the one hand, with
a Pt and a Rh catalyst on the other hand. For the dissociation of nitric oxide, lower values for
both rate coefficients are found than the literature values. This means that at high
temperature, the current model will predict slower rates. The combination of a high pre
exponential factor and a relative low activation energy, used by the work of Oh, will cause
the nitric oxide dissociation to be almost instantaneous already at quite low temperatures (> 500 K). The steps involving N₂O are somewhat different in each model, making comparison
less relevant. The Sadhankar and Oh model again predicts higher rate coefficients than the
model used in this work.
Figure 5.10. Reactor outlet concentrations (markers, measurements; lines, model predictions) versus time for NO reduction in the presence of O₂ at a temperature of 523K and an oscillation frequency of 1/10 Hz.
A: CO, O₂ and NO concentrations
B: CO (left axis), N₂, N₂O and NO₂ (right axis) concentrations

Figure 5.11. Model predicted fractional surface coverages versus time on the noble metal (above), and on the ceria surface (ξ) and in the ceria sub-layer (ζ) (below) at 15 mm from the top of the catalyst bed, corresponding with the experiment of figure 5.10 (the fractions of N* and N₂O* are too small to visualise)
The model enables prediction of the fractional surface coverages of species on the catalyst. Figure 5.11 (above) shows the surface coverages of the noble metal and of the alumina support versus time at the end of the reactor, while figure 5.11 (below) shows the coverages of the ceria surface and the ceria sub-layer. At the end of the rich half-cycle (t = 11 s), the noble metal and ceria surfaces contain mainly CO. The ceria sub-layer contains O species and some residual NO and NO2 species. As soon as the switch to the lean half-cycle is made (t = 11 s), some CO desorbs from the noble metal, while oxygen and NO will adsorb onto it. Some of the desorbed CO may re-adsorb onto O* to give OCO* species (step 6). Adsorbed oxygen adatoms react fast with CO on noble metal and more slowly with CO on ceria to give
gaseous CO$_2$. The coverage of O* rises almost instantly forcing NO adsorption onto O* to give NO$_2$*. A large part of NO is adsorbed by the ceria surface and passed on toward the sub-layer. NO from the previous half-cycle, that did not desorb, dissociates, using the vacant sites generated by CO oxidation. When all CO has been removed from the noble metal, ceria becomes filled with oxygen (t = 12 s). The O* surface coverage passes through a maximum (t = 12.5 s) due to NO adsorption on O* to form NO$_2$* (step 19). As the forward adsorption step is not activated, while the backward desorption step is, NO$_2$* species will inhibit CO oxidation at low temperatures. The increase of the NO$_2$* surface coverage and the filling of the ceria with NO continues until the switch from lean to rich is made at t = 16 s. If a lower switching frequency would be used, much more NO would adsorb onto the catalyst.

As soon as the switch to the CO in He feed has been made, a front of massive NO desorption travels through the reactor. This causes a temporary higher NO gas phase concentration, leading, at first, to a sudden increase of NO species on the catalyst downstream of the front (t = 16.5 s). When the front has left the reactor, the NO coverages at the end of the reactor decrease (t = 17 s), and the NO desorption peak decays. Some NO in the gas phase is able to adsorb onto the noble metal, and partly dissociates to give N$_2$O and N$_2$. This is caused by the relative large number of vacant noble metal sites created by CO oxidation. The oxygen is subsequently very rapidly removed from the noble metal and ceria (t = 17.5 s) and replaced by adsorbed CO. Only the species from the ceria sub-layer are consumed much slower, resulting in quite a large CO$_2$ tail (figure 5.10, t = 19-21 s). The fractional coverages of N and N$_2$O are very low during the entire period, which indicate that N$_2$ and N$_2$O formation and desorption are relatively fast compared to NO dissociation.

The modelling results at 548 and 573 K, not shown, indicate that the conversion of all components increases with temperature. Less N$_2$O is produced as it decomposes faster (step 17). Faster NO desorption leads to less NO storage on ceria. The capacity of the sub-layer (table 5.3) increases rapidly in this temperature range, clearly indicating the contribution of the ceria bulk.

5.6.2. NO reduction by CO in the absence of oxygen

Figure 5.12 shows the experimental and modelling results of a measurement where 0.5 vol.% CO was alternated with 0.1 vol.% NO at 523 K. Again, N$_2$, N$_2$O, and NO$_2$ are depicted on the right y-axis. It is observed that the conversion of NO to N$_2$ is much higher when O$_2$ is absent in the gas phase. A logical consequence is a smaller CO conversion. The model is reasonably able to describe the measured data with the same rate parameters, although the model predictions for concentrations of the N containing gases are not very accurate. All concentrations except CO and CO$_2$ are very low. The conversion of NO into N$_2$ is almost complete during the entire lean half-cycle; at the start some N$_2$O is produced, and at the end, some NO break-through occurs as CO is depleted.

The fractional catalyst coverages versus time are plotted in figure 5.13. During the rich half-cycle the surface is mainly covered with CO, while during the lean half-cycle the surface is rather empty. This large fraction of vacant noble metal sites allows rapid dissociation of NO*, hence leading to a large formation of N$_2$. For the formation of N$_2$O, both N* and NO* are required next to each other on the noble metal surface. This only occurs at the beginning and end of the lean half-cycle, where little inhibition of the NO dissociation takes place. The fractional surface coverage at the end of the reactor is very low for most species, and therefore cannot be seen in figure 5.13. At t = 19.5 s, some NO* can be seen on the noble
metal surface. This indicates that, after the switch to the rich feed, NO at the begin of the reactor has desorbed and has re-adsorbed at the end of the reactor.

At the start of the lean half-cycle ($t = 11$ s), still quite large amounts of CO are present on the catalyst and at the end oxygen starts to accumulate on the noble metal surface. This cannot be seen from figure 5.13, because the model does not predict that the oxygen reaches the reactor outlet at this frequency. At higher temperatures, similar phenomena as at 523 K are observed.

5.7. Conclusions

Various constituents of the commercial Pt/Rh/CeO$_2$/γ-Al$_2$O$_3$ catalyst have been studied separately with respect to the transient reduction of NO by CO in the presence and absence of oxygen. This comparison of several model catalyst formulations is a successful approach for understanding complex industrial catalysts. The transient experiments provided new mechanistic insights, such as: reversible adsorption of NO on ceria appeared independent of the oxidation state of ceria, indications of bulk diffusion of NO into ceria, ceria cannot dissociate NO, but can store O atoms from NO dissociating on the noble metal.

Chemisorbed CO does not directly react with chemisorbed NO, but leads to additional desorption of NO through cross-desorption. N$_2$ and N$_2$O formation only occur after NO dissociation, which is inhibited by the presence of oxygen, and the main path for N$_2$ formation proceeds by N$_2$O decomposition. The reduction of gaseous N$_2$O proceeds slower than the reduction of NO, because of slow N$_2$O adsorption. The presence of Rh in the catalyst accelerates the rate of certain reaction steps, but does not alter the mechanism. A high resolution mass spectrometer proved to be a very useful tool for transient experiments, in which isobaric masses occur.

The kinetic model is able to predict adequately the experimental data for both rich and lean half cycles with one set of rate parameters. The catalyst has a very large storage capacity for NO, however the presence of oxygen inhibits the dissociation of NO, which is necessary for N$_2$ formation. Both NO and O are stored on the catalyst during the lean half-cycle and released or reduced during the rich part. NO$_2$ formation on the catalyst inhibits the CO oxidation as well as the NO reduction. At the relatively high temperatures used here, effects as CO spill-over from noble metal to ceria and sub-surface ceria oxidation and reduction by both NO and O become important.

References

Kinetics of nitric oxide reduction

29, 550
Huinink J.P., PhD Dissertation, Eindhoven University of Technology, 1995
DEVELOPMENT OF A KINETIC MODEL FOR THE PREDICTION OF TRANSIENT COLD START BEHAVIOUR OF A COMMERCIAL AUTOMOTIVE EXHAUST GAS CATALYST

The work in this Chapter will be submitted to Applied Catalysis B, Environmental

Abstract
A kinetic model for a commercial automotive exhaust gas catalyst has been developed on the basis of elementary reaction steps. This model involves the oxidation of CO, C\textsubscript{2}H\textsubscript{2}, and C\textsubscript{2}H\textsubscript{4} as well as reactions of NO to NO\textsubscript{2}, N\textsubscript{2}O, and N\textsubscript{2}. The kinetic model is capable of predicting catalyst surface coverages and gas phase concentrations in time and along the axial reactor axis during transient cold-start experiments, performed with feed-cycling of synthetic exhaust gases in a laboratory fixed-bed reactor over a Pt/Rh/CeO\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3} catalyst. The model is based on elementary reactions steps, which were acquired partly from literature and partly from analysis of the experiments.

The model shows explicitly the important influence of ceria, like O\textsubscript{2} and NO storage, as well as bifunctional reactions involving the noble metal and the ceria surface. These latter reactions concern CO, C\textsubscript{2}H\textsubscript{4}, and C\textsubscript{2}H\textsubscript{2} oxidation and ceria assisted NO dissociation.

The model is verified on the basis of a number of independent experiments performed at conditions close to real-life automotive exhaust catalysis. The model is able to accurately predict these kinetic experiments, but it still lacks a number of steps, necessary to predict real-life experiments, e.g. engine-bench. One of these is the influence of high concentrations of carbon dioxide and water, which both adsorb on the ceria surface. Generally, carbon dioxide has an inhibiting influence, while water has a very large rate enhancing effect.

6.1. Introduction

The continuous expansion of road traffic causes an on-going demand for less pollution from automotive engines, reflected by increasingly severe legislation (Shelef & McCabe, 2000; Greening, 2000; Bertelsen, 2000). The pollutants are toxic and contribute to the formation of smog and acid rain, and may also lead to an increase of the greenhouse effect. The removal of these harmful components is commonly achieved by the application of a so-called three-way catalytic converter. These converters allow a simultaneous conversion of hydrocarbons, carbon monoxide, and nitrogen oxides into carbon dioxide, water, and nitrogen, and are very effective at stoichiometric feed conditions once the catalyst has reached a sufficiently high temperature (Taylor, 1993; Tamaru & Mills, 1994). Under cold start conditions, i.e. before the light-off of the monolith, the currently employed converters cannot eliminate all
pollutants. The low temperature of the catalytic surface means that the reaction kinetics are too slow to achieve full conversion of all pollutants (Zygourakis, 1989) - conversion of all pollutants is determined completely by the chemical kinetics.

A detailed understanding of the relevant reaction mechanisms and kinetic processes, taking place simultaneously and interactively at cold-start conditions, could assist in optimisation of the catalytic converter and/or the catalyst formulation, as well as in the development of new control strategies (Balenovic et al., 1999). Using the kinetic model, an optimal motor management system can be developed, in order to reduce emissions still further. Optimal emission reduction may be achieved when the Oxygen Storage Capacity (OSC) is only partly filled at all times, since both oxidation as well reduction reactions can then take place simultaneously. The filled fraction can, however, not be measured directly. A controller, which contains a model of the catalytic converter, is able to calculate the degree of OSC filling. As such, the model acts as a soft sensor, using available sensor data as the only external input. The value of the lambda parameter ($\lambda$), i.e. the relative air/fuel ratio compared to stoichiometry, before the catalyst is used to calculate the OSC filling, while the value of the $\lambda$ sensor behind the catalyst is used for updating the model to account for catalyst deactivation. On the basis of the model, the engine can be controlled extremely tightly in order to obtain the desired behaviour, i.e. optimal conversions. Since model errors will be immediately transferred into controller errors, very accurate and stable models are necessary.

Such models require knowledge of the intrinsic transient kinetics on the basis of elementary reaction steps, because of the dynamic character of the converter operation. During catalyst warm-up especially, the operating conditions change continuously, resulting in alterations of the rate-determining step (Silveston, 1995). Moreover, oscillations of the reactor feed composition with frequencies of about 1 Hz (Taylor & Sinkevitch, 1983), as induced by the currently applied lambda controller, cause transient effects that influence the time-averaged conversion due to the non-linear character of the kinetics (Herz, 1981). Finally, the behaviour of the driver introduces transient phenomena, and these are usually accounted for by typical tests like FTP and European driving cycles. It affects the converter performance via the space velocity and the exhaust gas temperature.

An enormous amount of publications is available about reaction mechanisms and catalyst characterisation. Kinetic studies, however, have been reported much less. This especially holds for kinetic models with all three major reactions involved in three-way catalysis. Voltz et al. (1973) were the first to present a kinetic model based on the three global reactions, over a Pt/Al$_2$O$_3$ catalyst. The conversion of nitric oxides was not yet considered important, as the model does incorporate the presence of nitric oxide, but does not allow to calculate its conversion. Since no rhodium and ceria are present in the catalyst, the nitric oxide conversions will not be high. The model is based on steady state experiments and predicts rates from Langmuir Hinshelwood type of equations, i.e. not on the basis of elementary steps.

The model from Voltz et al. (1973) is used by different authors for transient calculations. Pattas et al. (1994) expanded the Voltz model with transient data about storage and release of oxygen on ceria, present in their catalyst. This semi-transient model is then used for monolith calculations, in order to describe their transient experiments. The difference in catalysts is accounted for by changes in the kinetic rate parameters. The model consists of the following global reactions:

$$\text{CO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2$$ (1)
Development of a kinetic model

C₃H₆ + 9/2 O₂ → 3CO₂ + 3 H₂O  \hspace{1cm} (2)
C₃H₈ + 5O₂ → 3 CO₂ + 4 H₂O  \hspace{1cm} (3)
H₂ + ½ O₂ → H₂O  \hspace{1cm} (4)
CO + NO → CO₂ + N₂  \hspace{1cm} (5)

The storage and release of oxygen on ceria is considered as follows:

2CeO₂ ↔ Ce₂O₃ + ½ O₂  \hspace{1cm} (6)

This model is able to predict adequately conversions and light-off behaviour of their tested catalysts. Tuning of the rate data enables to describe different catalysts.

Another model, partly based on the Voltz model, is presented by Siemund et al. (1996). Additions have been made, using work from Oh & Cavendish (1982) and Subramanian & Varma (1984, 1985). Some parameters were adapted manually in order to obtain better results. The authors mention that some inadequate descriptions of their measured data are partly due to the simplicity of their used model. This especially holds for their transient data. A similar model by Dubien & Schweich (1998), based on Voltz et al. (1973) and Subramanian & Varma (1985), where the propylene oxidation has been replaced by methane oxidation (Bart, 1992), is used for the prediction of light-off curves.

The reaction steps 1-5 as listed above have also been used by Jirát et al. (1999), in order to predict conversions of lean burn exhaust gases over a Pt/CeO₂/BaO catalyst. The following steps from Koltsakis et al. (1997) have been added to account for oxygen and nitric oxide storage effects:

½ O₂ + Ce → CeO  \hspace{1cm} (7)
CO + CeO → CO₂ + Ce  \hspace{1cm} (8)
NO + BaO → BaO-NO  \hspace{1cm} (9)
CO + BaO-NO → CO₂ + ½ N₂ + BaO  \hspace{1cm} (10)

This semi-empirical model is derived assuming the pseudo-steady state approximation for the surface coverages and is used to calculate several transient phenomena, encountered under automotive conditions, but these are not verified with measurements. Montreuil et al. (1992) presented a semi-empirical steady state model for a Pt/Rh catalyst and an exhaust gas consisting of carbon monoxide, two different hydrocarbons, hydrogen, oxygen, nitric oxide and ammonia. The model can adequately predict the steady state conversions of the considered components.

A model based on elementary reaction steps, i.e. not empirical, is composed from various literature data by Nievergeld et al. (1997). This model contains the following reaction steps:

CO + * ↔ CO*  \hspace{1cm} (11)
O₂ + 2* → 2O*  \hspace{1cm} (12)
NO + * ↔ NO*  \hspace{1cm} (13)
C₂H₄ + 2* ↔ C₂H₄**  \hspace{1cm} (14)
C₂H₂ + 4* ↔ C₂H₂****  \hspace{1cm} (15)
NO* + * → N* + O*  \hspace{1cm} (16)
CO* + O* → CO₂ + 2*  \hspace{1cm} (17)
In this case a '*' denotes a site on the noble metal. Oxygen storage is not accounted for, as all steps proceed over noble metal sites. Nitrogen is the only product from nitric oxide reactions, while N₂O and NO₂ are not considered as possible products. The steps and rate parameters were taken from different studies (CO/NO/O₂ kinetics from Oh et al., 1986; C₂H₄ from Sant & Wolf, 1989). Kinetics of acetylene oxidation were not available, so they adapted the ethylene oxidation model from Sant & Wolf (1989) with data from Mabilon et al. (1995). All data were obtained over different catalysts, even with different noble metals, which is a serious compromise. The work of Nievergeld et al. (1997), however, is the first study based on elementary reaction steps, and demonstrates the power of the approach. It should be noted, however, that the oxidation steps for the hydrocarbons (steps 14, 15, 20 and 21) are not elementary, but it is assumed that the oxygen assisted abstraction of the first hydrogen atom is rate determining in these steps. The kinetic model is inserted into a monolith model, and light-off and cyclic feeding simulations are shown, which at least show a qualitative agreement with generally observed phenomena.

This Chapter reports a transient kinetic model for an automotive exhaust gas, which describes the conversion of C₂H₄, C₂H₂, CO, O₂, and NO into H₂O, CO₂, N₂, N₂O, and NO₂ over a single commercial Pt/Rh/CeO₂/γ-Al₂O₃ three-way catalyst. This model has been obtained by adding separate sub-models, developed for the same catalyst, concerning the oxidation of CO (Nibbelke et al., 1998), C₂H₄ (Chapter 3), and C₂H₂ (Chapter 4), as well as the reduction of NO by CO in the presence of oxygen (Chapter 5). The combined model predictions will be compared to cyclic feeding experiments at which NO and O₂ in He is alternated with CO, C₂H₄, and C₂H₂ in He.

Furthermore, model predictions will be compared with experiments alternating a feed with a mixture where lambda equals 0.95 with a similar mixture where lambda equals 1.05 with an oscillation frequency of 1 Hz. This is done at both isothermal and heating conditions. The conversion of diesel/lean burn exhaust gases is considered by comparing experiments and model prediction at similar conditions, but with a much larger oxygen partial pressure, which was around 5 kPa. Finally, model predictions are compared with measurements from engine bench tests, using real exhaust gases, performed at dmc² (Hanau, Germany).

By means of separate experiments, the influence of large quantities of CO₂ and H₂O on the performance of the catalyst is investigated. Automotive engine exhaust gases contain 10-14 vol. % water and carbon dioxide. Qualitative suggestions for future expansion of the model in order to implement these effects will be given.

6.2. Experimental

The experimental set-up, used for the transient kinetic experiments is described in Chapter 2. Online, real-time analysis is performed with a Jeol JMS GCMate magnetic sector mass spectrometer, which allows to distinguish between the isobaric masses of CO/N₂/C₂H₄ and CO₂/N₂O. The experiments without acetylene in a reactor feed have been measured with a sampling frequency of 25 Hz, while the experiments with acetylene in the feed have been
measured at a sampling frequency of 48 Hz. All experiments were carried out under conditions for intrinsic chemical kinetics, when judged with well-known criteria that were developed for steady-state kinetic research. For the majority of the data, the intrinsicity is not affected by cycling of the feed (Hoebink et al., 1999), although this cannot be guaranteed in the short time after switching from one feed to the other. The range of experimental conditions used in this study is depicted in table 6.1.

The engine bench tests have been performed at dmc² (Hanau, Germany) using a 1.9L BMW gasoline engine operated at 3000 rpm. Measured are the concentrations of hydrocarbons, carbon monoxide, the total amount of NOx, and the catalyst temperatures both in front of and behind the catalyst at a sampling frequency of 1 or 2 Hz. The catalyst is the same Pt/Rh/CeO₂/γ-Al₂O₃ catalyst as used for the modelling in this thesis. In this case it was impregnated on a standard ceramic monolith, as currently used for exhaust gas catalysts, (15 cm long and 10 cm diameter) with a concentration of 170 gcat/monolith. The cell density equals 64 cells/cm², the wall thickness equals 0.016 cm, the density of the substrate equals 1.8 kg/l, the density of washcoat 0.9 kg/l, and the thermal capacity is 1020 J/kgK. The thermal capacity determines the rate of warm-up during the cold-start period. The washcoat thickness equals 0.049 mm, and the channel diameter equals 1.04 mm. The tests consist of stoichiometric (λ = 1) and lean (λ = 1.15) light-off experiments (from T = 484 to 709 K), and lambda sweeps (from λ = 0.99 to 1.025) at 673 K. In the light-off tests the temperature is increased in time, while the inlet composition remains the same, and in the sweep tests the inlet air/fuel ration is slowly (with a frequency of about 500s) changed from rich to lean and back at a constant inlet temperature.

### 6.3. Construction of the full kinetic model

#### 6.3.1. Introduction

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<th>Temperature range:</th>
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</tr>
<tr>
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<td>Chapter 3</td>
<td>403 - 443 K</td>
</tr>
<tr>
<td>C₂H₂ (+ CO) + O₂</td>
<td>Chapter 4</td>
<td>503 - 543 K</td>
</tr>
<tr>
<td>CO + NO (+ O₂)</td>
<td>Chapter 5</td>
<td>523 - 573 K</td>
</tr>
<tr>
<td>CO + C₂H₄ + C₂H₂ + NO + O₂</td>
<td>this Chapter (6)</td>
<td>548 - 598 K</td>
</tr>
</tbody>
</table>

In Chapter 5, a model for transient reactions of NO to N₂, N₂O, and NO₂ over a Pt/Rh/CeO₂/γ-Al₂O₃ catalyst has been presented. This model was combined with the model for the transient oxidation of CO to CO₂ by Nibbelke et al. (1998), in order to quantitatively describe the lean transient reduction of NO by CO. In this section, an improved version of
these combined models is extended with the models for the transient ethylene oxidation (Chapter 3) and the transient acetylene oxidation (Chapter 4). Table 6.2 gives an overview of the temperature ranges used in the separate studies. Notice that especially the presence of acetylene and nitric oxide requires high temperatures.

6.3.2. Numerical calculations

The fixed-bed reactor is regarded as an ideal isothermal plug flow reactor, with a constant total molar flow rate along the catalyst bed. The reactor model consists of the continuity equations for
1) \( \text{C}_2\text{H}_4, \text{C}_2\text{H}_2, \text{O}_2, \text{CO}, \text{NO}, \text{N}_2, \text{N}_2\text{O}, \text{NO}_2, \text{and CO}_2 \) in the gas phase,
2a) surface species adsorbed on the noble metal surface,
2b) \( \text{CO}_2 \) adsorbed on the \( \gamma\)-\( \text{Al}_2\text{O}_3 \) support,
2c) oxygen and nitric oxide adsorbed on the ceria surface,
2d) oxygen and nitric oxide in the ceria subsurface layer.

The continuity equation for gas phase component \( i \) is as follows:

\[
\frac{\partial C_i}{\partial t} + \frac{1}{\tau} \frac{\partial C_i}{\partial z} = \frac{\rho_B}{\varepsilon_B} \sum_k L_k R_{k,i} \tag{6.1}
\]

The continuity equations for species \( j \) adsorbed on the noble metal surface, species \( n \) on the alumina support, and species \( m \) on the ceria surface can be written as follows:

\[
L_{\text{NM}} \frac{\partial \theta_j}{\partial t} = \sum_k L_k R_{k,j} \tag{6.2a}
\]

\[
L_{\text{OSC}} \frac{\partial \xi_m}{\partial t} = \sum_k L_k R_{k,m} \tag{6.2c}
\]

\[
L_{\text{SUP}} \frac{\partial \delta_n}{\partial t} = \sum_k L_k R_{k,n} \tag{6.2b}
\]

\[
L_{\text{CeB}} \frac{\partial \xi_m}{\partial t} = \sum_k L_k R_{k,m} \tag{6.2d}
\]

As the initial condition for Equations (6.1) and (6.2), the steady state solution corresponding to the experimental conditions during the rich feeding half cycle at the reaction temperature, was chosen.

The boundary condition for Equation (6.1) is:

\[
z = 0, \; t > 0, \; C_i = C_i^0(t) \tag{6.3}
\]

The experimentally measured reactor inlet concentrations were used to produce model predictions for the outlet responses. The reactor inlet concentrations of \( \text{CO}_2, \text{N}_2, \text{N}_2\text{O}, \text{NO}_2 \) and \( \text{H}_2\text{O} \) were always kept zero, except for some experiments where \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) have been added to the feed in order to investigate their influence on the reaction mechanism.

The net production rates in Equations (6.1) and (6.2) can be calculated from the rates of the elementary reaction steps in the reaction mechanism, considered in Table 6.4:

\[
R_{k,i} = \sum_p v_{i,p} r_{k,p} \tag{6.4}
\]
The reaction rates \( r_{k,p} \) of the elementary reaction steps are calculated via the law of mass action while restricting the adsorption capacity to a monolayer as a maximum.

Since the calculations started from the steady state solution as initial condition, they had to be carried out until a stable (periodic) solution was reached. The latter was usually the case after one cycling period.

A backward differentiation formula (BDF integrator) from the NAG Fortran library Mark 18, (1997), routine D02NHF, was used for calculating the steady state solution of Equations (6.1) and (6.2). The transient calculations were carried out using the Method of Lines (Schiesser, 1991). This method consists of discretisation of the space-derivatives by finite differences. The set of partial differential equations becomes a set of ordinary differential equations, ODE, which can be integrated in time by an ODE integrator. The first order space-derivatives, i.e. the convection terms in Equation (6.1), were discretised by so-called backward or upstream differentiation. The time-integration was carried out using a BDF integrator from the NAG Fortran library (NAG, 1997), routine D02NCF. The numerical calculations were carried out on a Silicon Graphics CRAY Origin2000 and on an 800 MHz AMD Athlon Linux PC.

Estimation of parameters was performed with a non-linear multi-response regression analysis of the measured outlet concentrations. The following objective function was minimised:

\[
S(\mathbf{b}) = \sum_{q=1}^{\nu} \sum_{i=1}^{n} w_{i,q} \left[ y_{i,q} - g_q(x_i, \mathbf{b}) \right]^2 \rightarrow \text{minimum}
\]  

(6.5)

Minimisation was achieved with a multi-response Levenberg-Marquart algorithm (Froment & Hosten, 1981; Boggs et al., 1992).

The calculations on the engine bench tests have been performed using the same kinetic model as presented in this chapter, combined with a monolith model, including mass and heat transfer phenomena as well as heat production by reaction. A detailed description of this monolith model and the used numerical techniques was published before (Balenovic et al., 1999). The most important equations from the monolith model are presented in appendix A.

6.3.3. Improvement of the NO-CO model

The model for the NO reduction by CO in the presence of \( O_2 \), as has been described in Chapter 5 of this thesis, has been improved in order to obtain a better description of the experimental data. The reversible spill-over of carbon monoxide from the noble metal surface to the ceria surface, and the oxidation of CO adsorbed on ceria by oxygen adsorbed on noble metal has been removed from the model. The main reason for introducing this step in Chapter 5 was the observed difference between Pt/Rh/Al\(_2\)O\(_3\) and Pt/Rh/CeO\(_2\)/γ-Al\(_2\)O\(_3\) for the amount of CO which could adsorb during the rich half-cycle. This difference appeared to be more than could be explained by stoichiometry only. On the other hand, a ceria surface covered by CO would give a dynamic behaviour different from the behaviour seen in many bench-experiments, since the function of the ceria would mainly be excluded in case of a CO covered ceria surface. For this reason the reversible CO spill-over has been removed from the model. The consequence of this removal is the need for a re-optimisation of the kinetic rate coefficients of the steps in Table 5.3 (Chapter 5). In the re-optimisation, especially the rate coefficients of the desorption of carbon monoxide (step 1b, table 5.2) and the Langmuir-
Hinshelwood reaction between adsorbed carbon monoxide and oxygen (step 4, table 5.2) had to be adapted for a better description in the temperature range 523-573 K. An adaptation of the other rate parameters was not required, since the rate coefficients of the corresponding reactions did not reach extremely high values at temperatures below 600 K.

Figure 6.1 shows a comparison between experimental CO oxidation data from Nibbelke et al. (1998), and the model predictions at 393 K using the new model coefficients. Compared to the model of Nibbelke et al. (1998) there are some differences. The rich half-cycle is still quite adequately predicted, especially the CO signal. The carbon dioxide peak is less steep and lower than in the experiment, which was also the case in the original model. In this half-cycle, the OCO-path, from which the rate parameters have not been changed, is most important.

The prediction of the lean half-cycle, however, has become worse. The slower desorption of the carbon monoxide at the end of the rich half cycle causes a too low adsorption rate of oxygen, resulting in a too large oxygen break-through peak. The carbon dioxide peak and the oxygen signal from the original model deviate from the experiments in a similar way, but to a lesser extent. For the application in practice of the complete kinetic model, it is more important to adequately describe the carbon monoxide oxidation at temperatures above 500 K, than below this temperature. This is because carbon monoxide will only react below 500 K if both acetylene and nitric oxide are absent, as was seen in Chapters 4 and 5, respectively. These conditions will rarely be met under real automotive conditions.

Improvement of the NO model, especially for the experiments without oxygen, was tried by addition of the following steps:

\[
\text{NO}^\ast + \text{N}^\ast \leftrightarrow \text{NCO}^\ast + \ast \\
\text{NCO}^\ast + \text{NO}^\ast \rightarrow \text{N}_2 + \text{CO}_2 + 2\ast
\]

The experiments described in Chapter 5 gave no direct evidence for the presence of such species on the noble metal surface, but such species have been identified via IR spectroscopy by Captain & Amiridis (1997) and Matyshak et al. (1995). They report that these species may react to give \( \text{N}_2 \) or \( \text{NO}_2 \), but the rates are quite low, and would therefore not contribute
significantly to the reactions. Indeed, after regression, the mentioned steps did not show significant effects. Therefore the steps were removed again from the model.

Another step added to the model was the following:

\[ \text{NOs} + * \rightarrow \text{N}^* + \text{Os} \]  (24)

This step is very similar to the bi-functional dissociation of NO as was already present in the model, but the difference is that in this case NO is adsorbed onto the ceria instead of onto the noble metal. Similar steps have been reported before (Cordatos & Gorte, 1996; Trovarelli et al., 1999; Diwell et al., 1990), which indicate that NO on the ceria can dissociate with the aid of the noble metal.

Figure 6.2 (on page 126) shows the results as an example of the improved NO-CO-O\(_2\) model at 523 K, which can be compared with Figure 5.10, depicting the earlier modelling results. The new rate coefficients can be found in Table 6.5. As can be seen, an improvement of the description of most components has been achieved. The predictions of the experiments without O\(_2\) were hardly changed with respect to the N-containing components. Especially the CO\(_2\) peak after the switch from the rich to the lean feed and the tail of the CO\(_2\) peak have improved considerably. The N-containing species have only slightly been improved. The CO desorption tail immediately after the switch to the NO-O\(_2\) feed (figure 5.10) has now disappeared, which is also an improvement. The O\(_2\) signal now shows an additional adsorption immediately after its break-through (\(t = 12 – 13\) s), which was not seen in the experiment. This is probably related to a relatively fast filling of the ceria sub-surface layer by oxygen from the ceria surface.

6.3.4. Extension of the model with ethylene oxidation

In this section, the model for the transient ethylene oxidation will be added to the formerly presented model for CO-NO-O\(_2\) reactions. In order to obtain sufficiently high conversions, the reaction temperature for experiments involving all model components had to be higher than for the oxidation of the individual rich components. This is especially the case for experiments with nitric oxide and/or acetylene present, which raises the light-off temperature of the gas mixtures with approximately 100-150 K. For example, an experiment where 0.15 vol.% ethylene in helium was alternated with 0.10 vol.% nitric oxide plus 0.40 vol.% oxygen in helium, hardly yielded any carbon dioxide at temperatures below 500 K. Hence, for the addition of the transient ethylene oxidation model to the CO-NO-O\(_2\) model, the rate parameters must be extrapolated over a temperature range of 150 K. This required adaptation of parameters. The rate parameters for the transient ethylene oxidation were adapted (if necessary) in such a way that accurate descriptions of experiments in the temperature range 523-573 K were obtained, while leaving the descriptions of experiments in the temperature range 393-443 K more or less unchanged, see Figure 6.3. Especially the lower activation energy of the new parameter cause the value of the rate parameter to become less temperature dependent. The experiments in the high temperature range consist of alternations between ethylene in helium versus oxygen and nitric oxide in helium, while the experiments in the low temperature range consists of alteration between ethylene in helium and oxygen in helium (Chapter 3).

Experiments, where ethylene in helium was alternated with nitric oxide in helium (i.e. without oxygen), did not show any conversion even at temperatures up to 573 K.
Furthermore, when switching from the lean to the rich feed, it was found from the carbon dioxide peak, that ethylene can react with oxygen adatoms on the ceria surface. At low temperatures (below 443 K, Chapter 3) this reaction was found to be insignificant, and was therefore not considered in the model from Chapter 3. In this case, $\pi$ ethylene on the noble metal reacts with six ceria surface oxygen adatoms to give carbon dioxide and water. At higher temperatures, as applied in this Chapter, the reaction between ethylene and oxygen from ceria becomes significant and is therefore included into the model.

![Figure 6.3. The natural logarithm of the rate coefficient for the desorption of ethylene, step 25b (tabl 6.5), versus the reciprocal temperature, using the original rate parameters (Chapter 3), black line, and the new rate parameters (grey line).](image)

**Figure 6.3.** The natural logarithm of the rate coefficient for the desorption of ethylene, step 25b (tabl 6.5), versus the reciprocal temperature, using the original rate parameters (Chapter 3), black line, and the new rate parameters (grey line).

![Figure 6.4. Experimental results (markers) and model predictions (lines) for an experiment alternating 0.15 vol.% $C_2H_4$ with 0.5 vol.% $O_2$ at a frequency of 1/10 Hz and a temperature of 423 K. The rate parameters used were presented in Chapter 3 with adaptations as shown in Table 6.3. The latter have been determined in this Chapter for the temperature range 523 - 573 K.](image)

**Figure 6.4.** Experimental results (markers) and model predictions (lines) for an experiment alternating 0.15 vol.% $C_2H_4$ with 0.5 vol.% $O_2$ at a frequency of 1/10 Hz and a temperature of 423 K. The rate parameters used were presented in Chapter 3 with adaptations as shown in Table 6.3. The latter have been determined in this Chapter for the temperature range 523 - 573 K.

Table 6.3 shows the original and the new values of the rate parameters which were changed to account for the temperature extrapolation. Table 6.5 shows all rate parameters used in this study. The model predictions at temperatures around 400 K have been recalculated with the new rate coefficients. They still compare reasonably to the measured data. As an example, the calculated rate coefficient for the desorption of ethylene is plotted versus the temperature in Figure 6.3, using the original and the new rate parameters. The lines cross near 423 K. Figure 6.4 shows an example of an experiment and the model calculation using the new rate parameters from Table 6.3. As can be seen, the description is only slightly less adequate than the description discussed in Chapter 3.
Figure 6.5 compares the predictions of a combined C$_2$H$_4$ and NO/O$_2$ model with an experiment, where 0.14 vol. % C$_2$H$_4$ is alternated versus 0.4 vol. % O$_2$ and 0.1 vol. % NO. This experiment was performed at a temperature of 548 K and an oscillation frequency of 1/10 Hz was used. The markers represent the measurements and the drawn curves show the model predictions, obtained with the adapted parameters shown in Table 6.3. In general, an adequate description of the experimental data by the model is given. The carbon dioxide peaks as well as the oxygen signal including the break-through peak and the ethylene signal are very well predicted. The N$_2$ and N$_2$O signals are reasonably well predicted, while the NO$_2$ prediction is not very accurate, as was already seen in the CO-NO model as well. The model predicts somewhat more nitrogen and less nitrous oxide than was found in the experiment. This is strongly dependant on the vacant sites produced by the oxidation of ethylene. When a large number of vacant sites is created, the production of N$_2$ is favoured over N$_2$O because the majority of the NO present on the noble metal surface will dissociate. Apparently, the model predicts a too fast formation of vacant sites.

The adsorption of nitric oxide, predicted by the model is less than observed in the experiment. This would indicate that the storage of oxygen and nitric oxide predicted by the model is too small, but a higher storage of these species in the model would also lead to larger CO$_2$ production and more ethylene consumption. This deviation leads also to an incorrect prediction of the desorption of NO, which is much less than was seen in the experiment. For the model calculations the following capacities have been found by regression: L$_T = 5.5 \times 10^{-3}$ mol/kg, L$_{INT} = 5.6 \times 10^{-3}$ mol/kg, L$_M = 5.6 \times 10^{-2}$ mol/kg, and $\theta_{CHx} = 0.66$.

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<th>Parameter</th>
<th>original value</th>
<th>new value</th>
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</tbody>
</table>

At the end of the ethylene half-cycle, the catalyst noble metal surface is expected to be rather fully covered with ethylene species. Ethylene will desorb to some extent after the switch from the rich to the lean feed has been made (t = 14 s). The sites that will become vacant because of the ethylene desorption, and vacant sites on the ceria surface will be covered by oxygen and nitric oxide. It can be seen, however, that the production of vacant sites is not fast enough to compensate the supply of oxygen, since the oxygen outlet concentration almost follows its inlet concentration in time. This can be caused by vacant sites consumption via the step where $\pi$ ethylene is converted to di-$\sigma$ ethylene. The oxygen, which did adsorb, will react with the ethylene species on the noble metal surface, yielding carbon dioxide. This will also create vacant sites, which will speed up the oxygen adsorption. This can be seen in figure 6.5, where the oxygen concentration passes a maximum and subsequently a minimum. This is caused by a temporary larger ability for oxygen to adsorb onto the catalyst. This "break-through peak" exactly follows the carbon dioxide production: the minimum in the oxygen signal coincides with the maximum in the CO$_2$ signal. As soon as the major part of the ethylene has been
oxidised, the noble metal surface will become filled with oxygen and nitric oxide species. Therefore, the amount of vacant sites will decrease, resulting in a decreasing adsorption rate.

Figure 6.2. Reactor outlet concentrations (markers, measurements; lines, model predictions) versus time for NO reduction by CO in the presence of O2 at a temperature of 523K and an oscillation frequency of 1/10 Hz. Left axis: CO, O2, CO2 and NO concentrations. Right axis: N2, N2O and NO2 concentrations.

Figure 6.5. Reactor outlet concentrations (markers, measurements; lines, model predictions) versus time for NO reduction by C2H4 in the presence of O2 at a temperature of 548 K and an oscillation frequency of 1/10 Hz. A: C2H4, O2, and NO concentrations. B: CO2 (left axis), N2, N2O and NO2 (right axis) concentrations.

The oxygen outlet concentration will relax towards its inlet concentration. The moments, during the experiment, where vacant sites are available, also allow the dissociation of nitric oxide into N and O adatoms. N adatoms can recombine or react with adsorbed NO to form N2 and N2O. As soon as the amount of vacant sites decreases, also the production of N2 and N2O
Development of a kinetic model

will stop. The catalyst has a large storage capacity for nitric oxide, as can be seen from the nitric oxide signal during the lean half-cycle, which slowly increases from an almost complete adsorption at the beginning of the half-cycle to almost hardly any adsorption at the end. As soon as the switch from the lean to the rich feed is made, ethylene will adsorb on the noble metal and remove the oxygen. Also the nitric oxide massively desorbs from the catalyst. The vacant sites, produced from the reactions, allow again some N₂ and N₂O to be formed. In this case the production of vacant sites is fast enough to allow initially complete ethylene adsorption. However, due to an unfavourable reaction stoichiometry surface oxygen is depleted quite rapidly, causing the ethylene concentration to approach its inlet level. The reduction of surface and sub-surface oxygen from the ceria causes the long tail in the carbon dioxide formation.

The results of the addition of ethylene to the CO-NO-O₂ model can be seen in Figure 6.6, which shows an experiment, where 0.1 vol. % NO and 0.4 vol. % O₂ in He is alternated versus 0.14 vol. % C₂H₄ and 0.25 vol. % CO in He over the Pt/Rh/CeO₂/γ-Al₂O₃ catalyst bed with a frequency of 1/10 Hz at 523 K. Again, the markers indicate the measured data and the drawn lines indicate the model predictions. An adequate description of the experimental data is given by the model. The largest differences between the experiment and the model concern the first part of the carbon dioxide peak when switching from the lean to the rich feed and the NO desorption peak when switching from lean to rich. Especially the ethylene, carbon monoxide and oxygen concentrations as well as the adsorption of NO and the carbon dioxide peak after the switch from the rich to the lean feed are well predicted. The N-containing products are reasonably well predicted, as was also the case in the experiments without CO (Figure 6.5).

In spite of the different temperatures, there are essentially not many differences between the experiment with CO, displayed in Figure 6.6, and the experiment without CO, shown in Figure 6.5. All N-containing components show the same type of concentration changes, although more NO is converted when CO is present. More CO than C₂H₄ is converted, which indicates that CO adsorbs stronger on the noble metal surface than C₂H₄, and because of a more favourable reaction stoichiometry, much more CO₂ is produced. Also, the bifunctional path for CO oxidation by ceria-oxygen, which is much faster than the corresponding reaction for C₂H₄, contributes largely to the additional formation of CO₂ in the experiment with CO compared to the experiment without CO. This may also be the cause of the increased NO conversion. The oxygen concentration does not show a "break-through peak" as was the case in the experiment without CO. This indicates that indeed, the surface is mostly covered with CO at the end of the rich half cycle, because the reaction between CO and O is fast enough to allow all oxygen to adsorb, thus avoiding the oxygen break-through peak. Hence, the oxygen is now able to fully adsorb onto the ceria and noble metal surface, and react with the present CO and C₂H₄. The CO₂ peak after the switch from lean to rich consists of two parts. The first part consists of a steep ascent followed by a steep descent, while the second part only consists of a slow descending part. From the CO and C₂H₄ signals, it can be seen that the first part of the CO₂ peak is caused by the combined oxidation of CO and C₂H₄ by noble metal oxygen, while the second part is mainly determined by the oxidation of CO by ceria-oxygen. For the model calculations the following capacities have been found by regression: \( L_T = 5.1 \times 10^{-3} \) mol/kg, \( L_{\text{INT}} = 3.3 \times 10^{-3} \) mol/kg, \( L_M = 6.0 \times 10^{-2} \) mol/kg, and \( \theta_{\text{CH}_x} = 0.27 \).

6.3.5. The full model
On the basis of the former sub-section, the kinetics of acetylene oxidation will be added to the model. This will result in the complete kinetic model. It was expected that changes to the
model for transient acetylene oxidation were not necessary, since the conditions needed to oxidise acetylene resemble the conditions used for the full model. All catalytic reaction steps have been summarised in Table 6.4. The rate parameters used for calculations with the complete model are listed in Table 6.5.

Figure 6.7 shows an experiment, where 0.10 vol. % NO plus 0.40 vol. % O₂ in He have been alternated with 0.12 vol. % C₂H₂, 0.16 vol. % C₂H₄ and 0.5 vol. % CO. No kinetic rate parameter values were changed. For the model calculations the following capacities have been determined by regression: \( L_T = 1.3 \times 10^{-2} \) mol/kg, \( L_{\text{INT}} = 6.0 \times 10^{-3} \) mol/kg, \( L_M = 2.2 \times 10^{-2} \) mol/kg, and \( \theta_{\text{CHx}} = 0.53 \). It is a serious drawback that the values of these catalyst properties have to be determined by means of regression, but it is not possible to obtain these values from off-line experiments in a simple way, as has been explained in Chapter 3. Also in this case, the model is qualitatively able to predict the measured transients.

As can be seen from Figure 6.7, at the end of the rich half-cycle (e.g. \( t = 23 \) s), the outlet concentrations of all rich components (i.e. C₂H₄, C₂H₂, CO) have reached the same level as their corresponding inlet concentrations. As a result of this, the CO₂ production has become zero, and the noble metal surface will be fully covered by rich species, mainly acetylene. After the switch to the lean feed (i.e. O₂ and NO) is made, the feed of rich components is immediately directed to the exhaust. Some of the rich components will desorb to a minor
extent, yielding vacant sites for O_2 and NO adsorption. Also, the ceria, which had been reduced by the rich components, has sites available for O_2 and NO. This will start the combustion reactions, cleaning most of the rich components from the noble metal surface. Initially, this does not proceed fast enough for all oxygen to adsorb, resulting in a breakthrough of O_2 at the end of the reactor. As the reaction proceeds, more and more vacant sites are created, enabling more oxygen adsorption onto the catalyst surface, which can be seen by the temporary minimum in the O_2 signal.

A similar phenomenon can be seen for NO. The model has not predicted the very small NO break-through peak, and predicts an early break-through, without a peak, for O_2. As a result of this, the predicted CO_2 peak is too sharp and too early, compared to the experiment. Especially the rates of desorption of the rich components determine the break-through behaviour of oxygen, since these steps are responsible for creating vacant sites for O_2 to adsorb on. A lower desorption rate for acetylene might improve the prediction of the oxygen break-through peak. It can be seen that the minimum in the O_2 signal coincides with the maximum of CO_2 and N_2 production. At this time, about 25 s, the reaction rates have reached a maximum: CO_2 is produced at the highest rate and therefore the O_2 consumption is highest. Also, at this same moment, the fraction of vacant sites is maximum, leading to an optimum in the production of N_2. The amount of produced nitrogen is reasonably well predicted, but the signal still has a different shape. This is also caused by the incorrect prediction of the oxygen
break through. After the switch from the rich to the lean feed, the amounts of rich species on the noble metal start to decrease. At the maximum CO₂ production, the ratio of rich and lean components on the catalyst is optimal. Immediately thereafter, the lack of rich components will cause the CO₂ production to decrease. All components, which can be oxidised relatively easily, are converted now, leaving the refractory species on the surface, together with the lean species. The oxidation of these refractory species yields the long and slow declining tail of the CO₂ peak, which is accurately predicted by the model. The O₂ and NO signals slowly relax towards their corresponding inlet concentrations.

<table>
<thead>
<tr>
<th>no.</th>
<th>Elementary reaction step</th>
<th>coefficient</th>
<th>no.</th>
<th>elementary reaction step</th>
<th>coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CO(\text{g}) + \text{\textit{a}} \leftrightarrow CO \text{\textit{a}}</td>
<td>k_{1}', k_{1}^b</td>
<td>6</td>
<td>OCO\text{\textit{a}} \rightarrow CO_{2} \text{\textit{a}}</td>
<td>k_{6}'</td>
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<td>2</td>
<td>O_{2}(\text{g}) + \text{\textit{a}} \rightarrow O_{2} \text{\textit{a}}</td>
<td>k_{2}^f</td>
<td>7</td>
<td>O_{2}(\text{g}) + s \rightarrow O_{2}s</td>
<td>k_{7}^f</td>
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<td>3</td>
<td>O_{2} \text{\textit{a}} \rightarrow 2O \text{\textit{a}}</td>
<td>k_{3}^f (=\infty)</td>
<td>8</td>
<td>O_{2}s + s \rightarrow 2O_{s}</td>
<td>k_{8}^f (=\infty)</td>
</tr>
<tr>
<td>4</td>
<td>CO + Os \rightarrow CO_{2}(\text{g}) + 2 \text{\textit{a}}</td>
<td>k_{4}^f</td>
<td>9</td>
<td>CO + Os \rightarrow CO_{2}(\text{g}) + \text{\textit{a}} + s</td>
<td>k_{9}^f</td>
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<tr>
<td>5</td>
<td>CO_{2}(\text{g}) + O* \leftrightarrow OCO *</td>
<td>k_{5}^f, k_{5}^b</td>
<td>10</td>
<td>CO_{2}(\text{g}) + \gamma \leftrightarrow CO_{2} \gamma</td>
<td>k_{10}^f, k_{10}^b</td>
</tr>
<tr>
<td>11</td>
<td>NO_{2}(\text{g}) + s \leftrightarrow NO \text{\textit{a}}</td>
<td>k_{11}^f, k_{11}^b</td>
<td>20</td>
<td>NO_{2} \text{\textit{a}} \leftrightarrow NO_{2}(\text{g}) + \text{\textit{a}}</td>
<td>k_{19}^f, k_{19}^b</td>
</tr>
<tr>
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<td>NO_{2}(\text{g}) + Os \leftrightarrow NO_{2}s</td>
<td>k_{12}^f</td>
<td>21</td>
<td>NO* + s \rightarrow N* + Os</td>
<td>k_{20}^f</td>
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<tr>
<td>13</td>
<td>NO(\text{g}) + \text{\textit{a}} \leftrightarrow NO *</td>
<td>k_{12}^f, k_{12}^b</td>
<td>22#</td>
<td>NOs + s \rightarrow N* + Os</td>
<td>k_{21}^f</td>
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<tr>
<td>14</td>
<td>NO* ++ \rightarrow N* + O*</td>
<td>k_{13}^f</td>
<td>23</td>
<td>Os + m \leftrightarrow s + Om</td>
<td>k_{22}^f, k_{22}^b</td>
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<td>15</td>
<td>NO* + N* \rightarrow N_{2}O* +++</td>
<td>k_{14}^f</td>
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<td>NOs + m \leftrightarrow s + NOm</td>
<td>k_{23}^f, k_{23}^b</td>
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<td>N_{2}O* \rightarrow N_{2}O(\text{g}) + *</td>
<td>k_{15}^f</td>
<td>25</td>
<td>NOs + Om \leftrightarrow s + NO_{2}m</td>
<td>k_{24}^f, k_{24}^b</td>
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<td>N_{2}O* + \rightarrow N_{2}(\text{g}) + O*</td>
<td>k_{16}^f</td>
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<td>18</td>
<td>N* + N* \rightarrow N_{2}(\text{g}) + 2 *</td>
<td>k_{17}^f</td>
<td>27</td>
<td>NO_{2}s + m \leftrightarrow Os + NOm</td>
<td>k_{25}^f, k_{25}^b</td>
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<td>19</td>
<td>NO(\text{g}) + Os \leftrightarrow NO_{2} *</td>
<td>k_{18}^f, k_{18}^b</td>
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<tr>
<td>20</td>
<td>C_{2}H_{4}(\text{g}) + 2* \leftrightarrow C_{2}H_{4} **</td>
<td>k_{24}^f, k_{24}^b</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>34</td>
<td>C_{2}H_{2}O* +50* \rightarrow 2CO_{2}(\text{g}) + 2H_{2}O_{(g)} + 6*</td>
<td>k_{29}^f</td>
<td></td>
<td></td>
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<tr>
<td>35#</td>
<td>C_{2}H_{4} +60Os \rightarrow 2CO_{2}(\text{g}) + 2H_{2}O_{(g)} + ++ 6s</td>
<td></td>
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</tr>
<tr>
<td>36</td>
<td>C_{2}H_{2}(\text{g}) + \text{\textit{a}} \leftrightarrow C_{2}H_{2} *</td>
<td>k_{31}^f, k_{31}^b</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>C_{2}H_{2} +2* \leftrightarrow C_{2}H_{2} ***</td>
<td>k_{32}^f, k_{32}^b</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>C_{2}H_{2} +30* \rightarrow 2CO ** + H_{2}O_{(g)} + 2*</td>
<td>k_{33}^f</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>C_{2}H_{2} ++++30* \rightarrow 2CO ** + H_{2}O_{(g)} + 4*</td>
<td>k_{34}^f</td>
<td>40</td>
<td>C_{2}H_{2}(\text{g}) + O* \leftrightarrow C_{2}H_{2}O *</td>
<td>k_{35}^f, k_{35}^b</td>
</tr>
<tr>
<td>41</td>
<td>C_{2}H_{2}O* +20* \rightarrow 2CO ++ + H_{2}O_{(g)} + *</td>
<td>k_{36}^f</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>C_{2}H_{2} +3Os \rightarrow 2CO ** + H_{2}O_{(g)} + 3s</td>
<td>k_{37}^f</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
As soon as the switch from the lean feed to the rich feed is made, all rich components are fully consumed by the catalyst during a small time interval, leading to a very high and sharp CO₂ production. This CO₂ peak as well as the concentrations of the rich components are very accurately predicted by the model. During this period most of the oxygen on the catalyst is consumed by the rich species. This proceeds much faster than during the switch from the lean to the rich feed, because the lean species adsorb rather easily on an oxygen-covered surface. The massive adsorption of rich species, in combination with the sudden stop in the feed of NO, results in a very large and steep cross desorption of NO from the noble metal and ceria surface. Also, some N₂ is produced during this very short and active time of oxidation reactions. The model does not predict the large desorption of NO, but predicts a too large production of nitrogen. This indicates that the dissociation of nitric oxide, predicted by the model, is too large. C₂H₄ adsorbs quite slowly, compared to C₂H₂ and CO. Therefore, this concentration will reach its inlet concentration first. Afterwards, still some C₂H₂ and CO adsorbs on the noble metal surface, which consumes oxygen from the catalyst, probably from the ceria, leading to the tail of the CO₂ peak.

Table 6.5. Estimates of the kinetic rate parameters belonging to the catalytic reaction steps listed in table 6.4. Steps k₃ and k₈ are assumed to be instantaneous (Nibbelke et al., 1998a). Step k₃₀ is set to a very low value for numerical model stability only (Nibbelke et al., 1998b). Dimensions k: m³/mol/s, A: s⁻¹, E, β: kJ/mol

| Step | Rate Constant | A₁₀ | A₁₁ | A₁₂ | A₁₃ | A₁₄ | A₁₅ | A₁₆ | A₁₇ | A₁₈ | A₁₉ | A₂₀ | A₂₁ | A₂₂ | A₂₃ | A₂₄ | A₂₅ | A₂₆ | A₂₇ | A₂₈ | A₂₉ | A₃₀ | A₃₁ | A₃₂ | A₃₃ | A₃₄ | A₃₅ | A₃₆ | A₃₇ | A₃₈ | A₃₉ | A₄₀ | A₄₁ |
|------|---------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| k₁   | 9.00 10⁶      |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| A₁   | 8.16 10⁹      |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| E₁   | 85.6          |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| β₁   | 4.15          |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| k₂   | 1.01 10¹      |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| k₃   | ∞             |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| k₄   | 1.81 10⁷      |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| E₄   | 60.6          |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| k₅   | 4.61 10¹      |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| A₅   | 248           |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| E₅   | 20.3          |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| A₆   | 20.5          |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| E₆   | 12.1          |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| k₇   | 11.1          |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| k₈   | ∞             |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| k₉   | 962           |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| k₁₀  | 11.0          |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |     |

More insight in the catalytic processes, taking place on the separate, active parts of the catalyst, can be obtained from the model predicted fractional surface coverages, plotted versus time in figure 6.8 for the same experiment as shown in figure 6.7.

According to the model, both the ceria surface as well as the ceria sub-surface layer become completely reduced during the rich half-cycle (e.g. t = 20 s). The noble metal surface is covered with CO* and the most reactive form of both hydrocarbons: π ethylene and π acetylene. As expected, more than half of the surface is covered by acetylene and only a small fraction is covered by ethylene. At the moment of the switch from the rich to the lean feed (e.g. t = 24 s), both CO* and C₂H₄* are rapidly converted into CO₂, but most of the C₂H₂* is converted into the more refractory C₂H₂***. First, the noble metal is filled with oxygen, while the ceria surface passes most of its oxygen on into the sub-surface layer. Once
This layer is filled, the ceria surface becomes occupied with oxygen. NO will adsorb both onto the noble metal and the ceria (sub)surface as NO₂.

Figure 6.8. Model predicted fractional surface coverages versus time on the noble metal surface, the ceria surface and in the ceria sub-surface layer for the experiment shown in Figure 6.7. The oxidation of C₂H₂, C₃H₄, and CO by NO and O₂ takes place at a temperature of 573 K and an oscillation frequency of 1/20 Hz. The surface coverages of NO*, N*, and others, not indicated in the figure, are too small (< 0.01) to visualise.

This explains the maximum in the noble metal coverage of oxygen (e.g. t = 25 s). After all π acetylene has either been oxidised or converted into di-σ+µ acetylene, the fraction of the latter species, which also occupies roughly half of the noble metal surface, starts to decrease. This occurs along two reaction paths: acetylene is oxidised to carbon monoxide, or converted back into π acetylene, which yield two vacant sites. The long tail of the carbon dioxide peak is explained by the model as the conversion of these species. Since decrease in the surface coverage of acetylene does not coincide with an increase of the coverage of oxygen species, it can be assumed that the acetylene species, which is being converted, mainly was present on the carbonaceous deposits, which are unavailable for oxygen. At the end of the lean half-cycle, di-σ+µ acetylene still covers more than 40% of the noble metal surface. At the moment of the switch from the lean to the rich feed (e.g. t = 34 s), di-σ+µ acetylene is rapidly converted to π acetylene. Additional acetylene and also ethylene and carbon monoxide can adsorb because vacant sites are created by the oxidation reactions. An initially high coverage of π ethylene decreases gradually, due to some cross-desorption by acetylene. This slow process continues throughout the entire rich half-cycle. NO₂ on the noble metal will decompose into oxygen adatoms and gaseous NO, causing the oxygen coverage on the noble metal to increase at first (e.g. t = 34 s). The coverages of NO* and N* are very low throughout the entire experiment. Therefore these have not been plotted in figure 6.8.

6.4. Qualitative assessment of the influence of high concentrations of water and carbon dioxide

In this section, an experiment performed at the same conditions as the experiment shown in figure 6.7, involving all model components, is compared in a qualitative way with experiments, where 10 vol.% water and/or carbon dioxide has been added to both reactor feeds. Real engine exhaust gases always contain high concentrations of water and carbon dioxide from the combustion processes taking place in the engine. On the basis of these experiments, it is the objective to present a set of elementary reaction steps, which should be able to qualitatively describe the effects of water and carbon dioxide.
Figures 6.9, 6.10 and 6.11 show the results of, respectively, the O₂, NO, and CO₂ outlet signals versus time for the following four experiments:
- "Nothing added": 0.5 vol.% CO + 0.15 vol.% C₂H₄ + 0.10 vol.% C₂H₂ versus 0.5 vol.% O₂ + 0.10 vol.% NO at 573 K and an oscillation frequency of 1/20 Hz.
- "Only CO₂ added": similar as the experiment above, only both feeds contain an additional 10 vol.% CO₂.
- "Only H₂O added": similar as the first experiment, only both feeds contain an additional 10 vol.% H₂O.
- "H₂O and CO₂ added": similar as the first experiment, only both feeds contain an additional 10 vol.% CO₂ and an additional 10 vol.% H₂O.

The concentrations of the other components do not vary very much when CO₂ and/or H₂O are added, and have therefore not been displayed. A high feed concentration of carbon dioxide prohibits the successful measurement of CO₂ transients during these experiments. This is why figure 6.11 does not show the influence of CO₂. Experimentally, it would be possible to measure the CO₂ transients if labelled O₂ (e.g. O¹⁸₂) would be fed during the lean half-cycle.

The influence of CO₂

In order to assess the influence of large concentrations of CO₂ the "Nothing added" experiment is compared to the "Only CO₂ added" experiment. In figure 6.9, it can be seen that oxygen cannot fully adsorb immediately, after a switch from a rich to a lean feed, resulting in the so-called oxygen break-through peak. The higher this peak is, the more difficult oxygen can adsorb on the catalyst. It can be seen that if only CO₂ is added to both feeds, oxygen displays the largest break-through peak. This indicates that CO₂ is able to inhibit the adsorption of oxygen by occupying sites on the catalyst. It has been found that CO₂ does not adsorb on noble metal sites (Engel & Ertl, 1979), but that it can adsorb on ceria (Li et al., 1989; Herz, 1981; Jin et al., 1987). The experiments without high concentrations have been carried out after the experiments with high concentration of CO₂ had been carried out, using the same catalyst batch. This indicates that the adsorption of CO₂ on ceria is reversible. Considering the high concentrations of CO₂, and the fact that CO₂ is present in both feeds, it is likely to assume that the adsorption/desorption of CO₂ on ceria is at equilibrium. The adsorption of CO₂ on ceria may indeed lead to inhibition of oxygen
adsorption on ceria: during the rich half-cycle, ceria oxygen will be consumed by carbon monoxide, ethylene and acetylene, creating vacant sites, which will be occupied by CO\textsubscript{2}. Due to the relative very large concentration of CO\textsubscript{2}, the coverage of CO\textsubscript{2} on ceria may be quite high. After the switch from the rich to the lean feed, part of the CO\textsubscript{2} has to desorb first, before oxygen can adsorb. It causes a competition between CO\textsubscript{2} and oxygen, which is won by oxygen because it does not desorb, while CO\textsubscript{2} does. This way the adsorption/desorption equilibrium of CO\textsubscript{2} is shifted towards gaseous CO\textsubscript{2}. However, this shift requires some time, leading to a large oxygen break-through peak. From the measured CO\textsubscript{2} signals (not shown) this cannot be verified due to the large noise in the MS signals.

Also NO adsorption is inhibited by the presence of CO\textsubscript{2} on ceria. In figure 6.10, the largest NO break-through peak is observed when 10 vol.\% CO\textsubscript{2} is added to both feeds. Since NO is able to adsorb in large quantities on ceria, as has been shown in Chapter 5, the inhibition of NO adsorption on ceria by CO\textsubscript{2} is completely similar to the inhibition of oxygen adsorption on ceria. The last part of the NO signals during the lean half-cycles show a strange behaviour. This is, however, not due to adsorption or reaction, but to experimental problems related to small pressure differences between both feed lines. This causes both inlet and outlet signals to deviate from the normally obtained square signals. Since for this qualitative analysis only the differences between the experiments are considered, this deviation from the optimal conditions is less important. Figure 6.10 does show that the large NO desorption peak is absent contrary to the experiment, where large concentrations of H\textsubscript{2}O and CO\textsubscript{2} are absent. This indicates that indeed much less NO can adsorb onto ceria, because of the presence of CO\textsubscript{2}. This also indicates that not all CO\textsubscript{2} is removed from ceria by adsorbing oxygen.

As mentioned before, the CO\textsubscript{2} signals cannot be interpreted because the produced CO\textsubscript{2} is hardly distinguished from the noise of the large amount of fed CO\textsubscript{2}. From the large oxygen break-through peak, it can be derived that the corresponding CO\textsubscript{2} production will be strongly delayed. Since CO\textsubscript{2} does not inhibit the adsorption of the rich components and since oxygen adsorption will remove some CO\textsubscript{2} from ceria, via cross desorption, the CO\textsubscript{2} peak after the switch from lean to rich is expected to be similarly shaped as the corresponding peak in the experiment without additional CO\textsubscript{2}. However, because of a possibly lower oxygen storage capacity, the carbon dioxide peak may be smaller. For modelling purposes, it should be sufficient to include the following adsorption and desorption step:

**Figure 6.10.** Reactor outlet NO concentration versus time for four experiments.

- **"Nothing added":** 0.5 vol.\% CO + 0.15 vol.\% C\textsubscript{2}H\textsubscript{4} + 0.10 vol.\% C\textsubscript{2}H\textsubscript{2} versus 0.5 vol.\% O\textsubscript{2} + 0.10 vol.\% NO at 573 K and an oscillation frequency of 1/20 Hz.
- **"Only CO\textsubscript{2} added":** both feeds contain an additional 10 vol.\% CO\textsubscript{2}.
- **"Only H\textsubscript{2}O added":** both feeds contain an additional 10 vol.\% H\textsubscript{2}O.
- **"H\textsubscript{2}O and CO\textsubscript{2} added":** both feeds contain an additional 10 vol.\% CO\textsubscript{2} and 10 vol.\% H\textsubscript{2}O.
The CO$_2$ produced during the experiments without high concentrations of CO$_2$, i.e. the experiments described in Chapters 3-5, may also adsorb onto ceria. The relatively low concentrations will hardly have any influence on the kinetics, but may change the shape of the CO$_2$ signals. This effect has been included into the model via the reversible adsorption of CO$_2$ onto the alumina carrier by Nibbelke et al. (1998). The corresponding rate parameters may be obtained from dedicated adsorption/desorption experiments using pure ceria.

**The influence of H$_2$O**

The influence of large concentrations of H$_2$O is investigated by comparing the "Nothing added" experiment with the "Only H$_2$O added" experiment. The influence of the presence of additional water is extremely high for the lean half-cycle. In figure 6.9 it can be seen that the oxygen break-through peak, which is present when no additional H$_2$O is added, has completely disappeared in the experiment where H$_2$O was added. Corresponding to this, the CO$_2$ signal after the switch from the rich to the lean feed (figure 6.11) shows a very high and sharp spike in the experiment where additional water has been added, whereas the experiment without additives shows a delayed CO$_2$ formation. The CO$_2$ peak after the lean to rich feed transition is slightly higher with less tailing.

From this, it can be concluded that the presence of H$_2$O enhances the production of CO$_2$. Such phenomenon has been observed before for CO oxidation as well (Kim, 1982; Hegedus et al., 1977; Chakrabarty et al., 1984; Muraki et al., 1991; Campman, 1996; Nibbelke et al., 1997), where it is found that the presence of oxygen is required since the used temperatures are too low for gas-phase water-gas-shift reactions to occur (< 700 K) (Whittington et al., 1995). Also, no hydrogen was found in these studies. Furthermore, it is known that H$_2$O does not adsorb onto a noble metal surface (Heras & Viscido, 1988; Peng & Dawson, 1977) but can adsorb on ceria (Sass et al., 1985; Padeste et al., 1993) and alumina (DeCanio, 1994; Cardona-Martinez & Dumesic, 1992). It is therefore assumed that water on ceria increases the availability of oxygen for the bifunctional path reactions. A less pronounced rate enhancing effect of H$_2$O for Pt/Al$_2$O$_3$ has also been found (Campman, 1996). It is assumed that in this case the alumina support plays a role similar to the ceria, providing oxygen for the combustion of CO. Hegedus et al. (1977) and Muraki et al. (1991) proposed that the presence of steam would alter the CO oxidation equilibrium, resulting in less CO inhibition, but Campman (1996) found evidence against this proposal.

Campman (1996) has performed steady-state CO oxidation experiments using H$_2^{18}$O and $^{16}$O$_2$, and discovered that most of CO is converted into C$^{16}$O$^{18}$O, where for each mol of this latter component also one mol of H$_2^{16}$O is produced. This indicates that steam is strongly involved in the oxidation of CO.

Campman (1996) proposes the following reaction scheme:

\[
\text{CO} + \ast \leftrightarrow \text{CO*} \quad (26)
\]
\[
\text{O}_2 + s \rightarrow \text{O}_2s \quad (27)
\]
\[
\text{H}_2\text{O} + s \leftrightarrow \text{H}_2\text{Os} \quad (28)
\]
\[
\text{H}_2\text{Os} + \text{Os} \leftrightarrow 2\text{OHs} \quad (29)
\]
\[
2\text{OHs} + \text{O}_2s \rightarrow 3\text{Os} + \text{H}_2\text{O} \quad (30)
\]
\[
\text{CO*} + \text{Os} \rightarrow \text{CO}_2 + s + \ast \quad (31)
\]
The combination of reactions 28-30 can be seen as a water assisted oxygen dissociation equivalent to:

\[ \text{O}_2s + s \rightarrow 2\text{Os} \quad (32) \]

This last step will proceed in the absence of water, but is said to be more slow than the combination of steps 28-30. Steps 28 and 29 are considered in equilibrium and very fast. This way the scrambling effect of the isotopes is explained. If steps 28-30 are combined, the rate enhancement would be explained by Campman (1996) as an increased dissociation rate of molecular oxygen on ceria.

There are two problems with Campman's proposal. First, a sequence of three serial steps (28-30), of which the third (step 30) is clearly not elementary, is assumed to be faster than one single elementary reaction step. This is at least unlikely. Second, Nibbelke et al. (1997, 1998) mention that the dissociation of O2s (step 32) is much faster than the adsorption of oxygen on ceria (step 27). This causes a low surface coverage of O2s, to be such that it becomes kinetically insignificant, and step 32 may be assumed instantaneous. Therefore it has no meaning to increase the rate of O2s dissociation, and it will not work in explaining the enhanced rate effect of water. Also in the context of the model, presented in this thesis, Campman's proposal will not work, since the adsorption steps for oxygen are directly taken from Nibbelke et al. (1998), who assumes instantaneous oxygen dissociation, as mentioned before.

It is clear that H2O indeed adsorbs on ceria. This can also be seen from figure 6.10, which shows that the adsorption of NO is inhibited by the presence of water, since a larger NO break-through peak is observed. However, unless oxygen is able to adsorb directly on a water covered ceria surface, ceria cannot be fully covered by water. This means that some type of adsorption/desorption equilibrium for water must exist, while a fraction of the ceria sites is vacant. In figure 6.9 the experiment with both CO2 and H2O in the feeds shows an oxygen break-through peak, while the experiments with only water added did not. This indicates that CO2 and H2O compete for the same ceria sites. In case both components are added, fewer vacant sites are available for oxygen adsorption. This leaves two possibilities: either the presence of water leads to a higher sticking coefficient of oxygen on ceria, or water is involved in the bifunctional path reactions. The only way that the sticking coefficient for the
adsorption of oxygen on ceria could be increased is via a type of Eley-Rideal step, where the oxygen from water is passed to di-oxygen:

\[ O_2 + H_2O^{18}s \rightarrow OO^{18}s + H_2O \]  

(33)

Apart from the fact that adsorption of O\(_2\) on H\(_2\)Os may be very unlikely, since two hydrogen atoms would have to be moved, such a step would not yield more than 50% ^18O, unless step 29 is still very important.

From the isotope experiments of Campman (1996), it is clear that water is involved in a chemical reaction since labelled ^18O from water ends up in CO\(_2\). Otsuka et al. (1983) gave evidence that H\(_2\)O can successfully oxidise ceria at 573 K with the release of gaseous hydrogen. Especially in the presence of noble metals, this reaction is very fast. The following equilibria are important:

\[ xH_2 + CeO_2 \leftrightarrow xH_2O + CeO_{2-x} \]  

(34)

\[ xCO + CeO_2 \leftrightarrow xCO_2 + CeO_{2-x} \]  

(35)

The rate enhancement by water could then be explained by the backwards reaction 34, which is a type of water-gas-shift reaction. However, in the experiments by Campman (1996), hydrogen was not observed. Also, in the current experiments, a continuous formation of CO\(_2\) during the entire rich half-cycle should be expected if reactions 34b and 35f were to be important. As can be seen from figure 6.11, in the second part of the rich half-cycle (e.g. t > 23 s) no CO\(_2\) is produced, despite the fact that both CO and H\(_2\)O are present in the gas phase. This indicates that O\(_2\) is also necessary, which was also found by Campman (1996). A possibility could be that reaction 34b would not yield gaseous hydrogen but cerium hydride.

This type of compound can be formed when large loadings of Ce in the presence of Pt and Rh are treated with hydrogen at 923 K (Chojnack et al., 1991). If oxygen is present, immediately water will be formed again, but if oxygen is absent, the ceria surface will be poisoned. In this way both the rate enhancement as well as the isotope effect and the oxygen requirement can be explained. In short:

\[ H_2O + s \leftrightarrow H_2Os \]  

(28)

\[ H_2Os + CO^* \rightarrow CO_2 + 2Hs \]  

(36)

\[ 2Hs + Os \rightarrow H_2Os \]  

(37)

Alternatively, OHs could be used as active species in a sequence:

\[ H_2O + s \leftrightarrow H_2Os \]  

(28)

\[ H_2Os + Os \leftrightarrow 2OHs \]  

(29)

\[ OHs + CO^* \rightarrow CO_2 + Hs \]  

(38)

In this way Os is required for the formation of OHs (step 29). Another possibility for the formation of OHs species could be a direct dissociation of water on ceria, instead of step (38):

\[ H_2Os + s \leftrightarrow OHs + Hs \]  

(39)
As far as is known, the cerium hydride species have not been investigated and/or observed during reaction conditions. Therefore no direct scientific evidence is available to support this mechanism. On the other hand, this mechanism is able to explain both the rate enhancing effect of water and the observed isotopic effect.

**The effect of both CO₂ and H₂O**

When high concentrations of both CO₂ and H₂O are added to the reactor feeds, the rate enhancing effect of water is partly cancelled by the inhibition of CO₂. The oxygen signal in figure 6.9 shows a break-through peak, which is smaller than the break-through peak in case no CO₂ and H₂O have been added. From the NO signal in Figure 6.10, H₂O seems to inhibit NO adsorption less than CO₂ does, but considerably less NO adsorbs than in case H₂O and CO₂ are absent. Only in the latter case the large desorption peak at the switch from lean to rich feed is observed. It can be concluded that the effects of water and carbon dioxide are completely different, and can be added separately to the model. For CO₂, a simple adsorption/desorption equilibrium will suffice, but modelling the effects of water is more complicated, leading to the need for more research.

### 6.5. Model verification

#### 6.5.1. Introduction

The full model, presented in section 6.3, is tested in a number of experiments at conditions closer to real automotive exhaust gas catalysis. This way, an impression is obtained about the capabilities of the model to predict conversions of real automotive exhaust gases. The experiments performed for this investigation are:

1. Feed oscillation around $\lambda = 1$ at 1 Hz.
2. Exhaust gas with high oxygen content, as met with diesel and lean-burn engines.
3. Engine bench tests: light-off and $\lambda$-sweep.

These experiments and their corresponding model predictions will be discussed in the next sections. In all experiments the capacities of the catalyst as well as the coverage of carbonaceous deposits have been optimised using regression analysis. This has been done because the values of these properties maybe different in each experiment, and are not easily accessible through means of dedicated experiments.

#### 6.5.2. Oscillation around $\lambda = 1$ at 1 Hz.

In a first experiment, alternating feeds with C₂H₄, C₂H₂, CO, NO and O₂ are applied in such a way that one feed gas has an air/fuel ratio of 0.91, while the other feed gas has an air/fuel ratio of 1.09. The following definition for the calculation of the air/fuel ratio ($\lambda$) was used:

$$\lambda = \frac{2 \times C_{O_2} + C_{NO} + C_{CO} + 2 \times C_{CO_2} + C_{H_2O}}{2 \times C_{CO} + 6 \times C_{C_2H_4} + 5 \times C_{C_2H_2} + 2 \times C_{CO_2} + C_{H_2O}} \quad (6.6)$$

The applied concentrations are listed in table 6.6. These mixtures are alternated over the reactor at a frequency of 1 Hz, and a fixed temperature of 573 K. This way, the exhaust of a car with a $\lambda$-controller driving at a constant speed is simulated. The $\lambda$-controller tries to keep the air/fuel ratio at unity, enabling oxidation and reduction processes to occur simultaneously. The temperature has been chosen as slightly below the light-off temperature of the catalyst.
This is not realistic for a car, but will ensure operation within the kinetically determined regime. The results of the experiment and the model predictions are shown in Figure 6.12. All concentrations oscillate between two steady states, which are both not fully reached because of the high frequency of the feed oscillations. This type of experiment clearly contains much less kinetic information than the experiments used to base the model upon. Carbon dioxide is the main product of the reactions. At the end of the lean half-cycle, CO₂ is at its minimum and at the begin of the rich half-cycle a maximum CO₂ production is reached. The time averaged fractional conversions of the inlet components are shown in table 6.6. The sequence of C₂H₂ (33 %), CO (20 %), O₂ (19 %), C₂H₄ (11 %), and NO (9 %) is as would be expected. Hardly any N₂ and N₂O are formed, indicating that the catalyst surface is almost fully covered during all time, making the dissociation of adsorbed NO very slow. Due to the continuous presence of O₂ and NO, a small amount of NO₂ is formed throughout the experiment.

The following capacities have been used for the model calculations of this experiment: L_T = 1.3 × 10⁻² mol/kg, L_INT = 6.0 × 10⁻³ mol/kg, L_M = 3.3 × 10⁻² mol/kg, and θ_CHX = 0.86. These values represent a large deactivation by carbonaceous deposits, and give the maximum values for the L_T and L_INT, as reported by Nibbelke et al. (1998).

It can be seen that the model predicts far more carbon dioxide than was observed in the experiment. The conversion of especially CO as predicted by the model is far larger than measured during the experiment. The predicted conversion of C₂H₄ is a little too high, while the predictions of C₂H₂ and NO are quite adequate. As a result of the too large CO conversion, also the predicted O₂ conversion is too high. The model predicts that the noble metal is covered with mainly C₂H₂ (~53 %), CO (~30 %), OCO (~12 %) and C₂H₄ (~4 %). The ceria surface is predicted to be mainly empty (~92 %) and the ceria sub-surface to be half filled (~66 %). The differences in surface coverages between the rich and lean half-cycles are very small.

The deviations between the experimental results and the model predictions are discussed, with emphasis on the too high conversion of CO into CO₂. At first, it has been checked whether the initial conditions (i.e. the feed concentrations at t = 0 s) for the model calculations were correct. In such complex kinetic systems the occurrence of multiple steady states is not uncommon. Therefore, another calculation was carried out which started with
five seconds of 0.1 vol. % C<sub>2</sub>H<sub>2</sub> fed over the reactor in order to assure a high initial coverage of the noble metal surface with both C<sub>2</sub>H<sub>2</sub> surface species. However, this did not change the model predictions significantly, indicating that both model calculations are stable and reach the same transient state.

Table 6.6. Reactor inlet concentrations during the 1 Hz switching experiments between rich and lean feeds. The right column shows the measured time averaged fractional conversions for the inlet components.

<table>
<thead>
<tr>
<th></th>
<th>rich</th>
<th>lean</th>
<th>conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1600 ppm</td>
<td>1500 ppm</td>
<td>11 %</td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>810 ppm</td>
<td>550 ppm</td>
<td>33 %</td>
</tr>
<tr>
<td>CO</td>
<td>0.49 vol. %</td>
<td>0.45 vol. %</td>
<td>20 %</td>
</tr>
<tr>
<td>NO</td>
<td>0.055 vol. %</td>
<td>0.08 vol. %</td>
<td>9 %</td>
</tr>
<tr>
<td>O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.79 vol. %</td>
<td>0.87 vol. %</td>
<td>19 %</td>
</tr>
<tr>
<td>CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.0 vol. %</td>
<td>0.0 vol. %</td>
<td>-</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.0 vol. %</td>
<td>0.0 vol. %</td>
<td>-</td>
</tr>
<tr>
<td>λ</td>
<td>0.91</td>
<td>1.09</td>
<td>-</td>
</tr>
</tbody>
</table>

A sensitivity analysis revealed that the large CO<sub>2</sub> production is due to the bifunctional path reaction, where CO on the noble metal reacts with O adsorbed on the ceria surface (i.e. step 9, table 6.4). Elimination of the mono functional Langmuir-Hinshelwood and the Eley-Rideal paths did not lead to significantly less CO<sub>2</sub> production. In fact, the elimination of the OCO* formation resulted in an even larger CO<sub>2</sub> production, indicating that OCO* inhibits the noble metal surface by means of its rather long residence time on the surface.

Further analysis indicated that the amount of CO adsorbed on the noble metal determines the rate of the bifunctional reaction path. A large decrease of the amount of ceria sites did not result in a lower predicted CO<sub>2</sub> production, while a large decrease of the amount of noble metal sites did. This means that an improved model prediction can be obtained if less CO would be adsorbed on the noble metal surface. This could be realised by increasing the desorption rate coefficient of CO, but would lead, however, to very improper predictions of the formerly described kinetic experiments, since the required increase of the mentioned parameter would have to be very high in order to obtain an adequate description of the experiment described in this section. The presence of large amounts of carbonaceous species cannot explain the observed lower CO conversion, since CO can adsorb onto these carbonaceous deposits. Another possibility to predict a lower amount of CO on the noble metal would be a decreased desorption of C<sub>2</sub>H<sub>2</sub>, which would lead to more competition between C<sub>2</sub>H<sub>2</sub> and CO for the noble metal sites. Calculations indicated that the rate coefficient for the desorption of C<sub>2</sub>H<sub>2</sub> had to be lowered by a factor 10 in order to obtain an adequate description of the 1 Hz experiment. This would lead to an inadequate description of the experiments shown in Figure 6.7: a CO break-through peak would result, which was not measured. A lower rate parameter of the bifunctional path itself, or a larger amount of OCO* would also lead to a better description of the 1 Hz experiment, but would seriously compromise the kinetic experiments in section 6.3.

Therefore, it seems likely that under the conditions of the experiment, a phenomenon becomes important which is not accounted for in the model. Such a phenomenon apparently causes a very large decrease of the catalyst activity. The influence on the CO oxidation is the highest, perhaps since CO oxidation is the fastest occurring reaction. A possible explanation might be the formation of less active noble metal oxides on the catalyst, which could be
described by the term "over-oxidation". In such processes, noble metal oxides are formed after a prolonged exposure of the catalyst to oxygen (Volokitin et al., 1986):

\[ \text{O}^* + \# \rightarrow \text{O}^{*\#} \]

Here, the \# indicates a site located in the sub-surface layer of the noble metal. The original noble metal surface site, however, is no longer as such available. The formed metal oxide (O^{*\#}) has a lower activity than the original oxygen surface species (O^*) (Carbello & Wolf, 1978; Burch & Hayes, 1995; Hiam et al., 1968), hence causing deactivation of the noble metal catalyst. The catalyst can be regenerated by slow reduction of the sub-surface noble metal layer, e.g. (Volokitin et al., 1986):

\[ \text{CO}^* + \text{O}^{*\#} \rightarrow \text{CO}_2 + \# + \ast \]

Similar steps for hydrocarbons could possibly also reduce the over-oxidised noble metal sites. Such mechanisms are often used to explain the occurrence of autonomous oscillations under atmospheric pressures (Hartman et al., 1994; Sales et al., 1982; Aluko & Chang, 1986).

Another possible explanation for the observed change in activity between the experiments where only one feed contains oxygen and the experiments where both feeds contain oxygen, could be the segregation of noble metals due to changes in the oxidation state of the noble metal surface. In a LEIS (Low Energy Ion Scattering) study of the Pt/Rh/\gamma-CeO_2/\gamma-Al_2O_3 and derived model catalysts, it was found that Pt and Rh in Pt/Rh/\gamma-CeO_2/\gamma-Al_2O_3 are present in the form of mixed clusters (Jansen et al., submitted). Beck et al. (1993) have shown that an oxygen covered surface of a mixed cluster in a Pt/Rh catalyst will become rapidly (order of tens of seconds) enriched with Rh. In the absence of oxygen the surface will become very slowly (order of hours) enriched with Pt. This could mean that during the experiments, where only one feed contains oxygen, the noble metal surface is enriched with Pt. During the experiments, where both feeds contain oxygen, the noble metal surface could then be enriched with Rh. If Rh is much less active than Pt in the oxidation of especially CO, then noble metal segregation could be an explanation for the observed change in activity. When rate coefficients of the noble metal reactions for the transient oxidation of CO by O_2 over Pt/\gamma-Al_2O_3 (Hoebink et al., 1999) are compared with the same steps over Pt/Rh/\gamma-CeO_2/\gamma-Al_2O_3 (Nibbelke et al., 1998), similar results are found. This means that the values of the rate parameters at 373 K differ less than a factor three. This could indeed mean that Rh does not contribute very much to the oxidation of CO over Pt/Rh/\gamma-CeO_2/\gamma-Al_2O_3. For modelling, it would implicate that separate Pt and Rh sites, including rates of segregation should be included into the model.

In order to verify the theory of noble metal over-oxidation, a number of experiments under various conditions have been carried out. First, steady-state experiments were performed using a fresh Pt/Rh/\gamma-CeO_2/\gamma-Al_2O_3 catalyst. During these experiments 0.15 kPa C_2H_4 and 0.55 kPa O_2 were co-fed to the reactor at a temperature of 423 K. Figure 6.13 shows the amounts of CO_2 measured by GC analysis, which can be considered as a degree for the catalyst activity. As can be seen, the initial activity decreases with the number of measurements (i.e. with time), until it has reached a stable activity. This is indicated in figure 6.13 by the diamond shaped markers, i.e. the first 19 experiments. After these experiments, the same catalyst batch was used for transient experiments at different cycling frequencies and temperatures. Before and after each day of transient experiments, a steady-state experiment,
under the above mentioned conditions, was carried out again. These experiments are indicated in figure 6.13 by experiment numbers 20 - 50. The triangle markers indicate the steady-state experiments performed before the transient experiments, and the square markers indicate the steady-state experiments after the transient measurements. As it appears, the steady-state experiments, performed after transient experiments show a higher activity, than the steady-state experiments, performed before the transients. Also, the activity of the catalyst during all these experiments (i.e. experiment # 20 - 50) is higher than the activity found after a long time of only steady-state experiments (i.e. experiment # 1 - 19).

The explanation may be that during the steady-state conditions, where continuously oxygen is being fed to the reactor, the catalyst becomes slowly over-oxidised. Under transient conditions, the oxygen half-cycles are too short to form sub-surface oxygen, or the coverages of C2H4 become too high for sub-surface oxygen to be formed. This indicates that the catalyst deactivates as soon as the steady-state mixture is fed to the reactor. As soon as the transient experiments begin, the activity increases, resulting in a higher CO₂ production. After a day of transient experiments, the activity is still high when the steady-state experiment is started. However, during this experiment the activity decreases again as can be seen from the experiment performed on the next day, before the start of a new series of transient experiments.

![Figure 6.13](image)

In order to verify a constant activity during the transient experiments, a standard experiment was chosen. In this standard experiment, 0.15 kPa C₂H₄ in He was alternated with 0.55 kPa O₂ at a frequency of 1/6 Hz. This experiment was carried out at random moments during one day of transient measurements at other cycling frequencies and temperatures. Figure 6.14 shows the results of all experiments, where the top of the highest CO₂ peak (after the switch from the rich to the lean feed, see Chapter 3) was chosen as a measure for the catalyst activity. The diamond shaped markers indicate the activity of the standard experiment, and the dots represent the "other" transient experiments. As can be seen, the activity of the "other" experiments differs quite a lot, due to the different conditions. The standard experiments all have the same activity, indicating that during the transient experiments the catalyst activity remains constant. This would mean that the formation of sub-surface oxygen is suppressed during the transient experiments.
Finally, a number of experiments was carried out, where transient and steady-state conditions were alternated, in order to observe the catalyst deactivation. The results are shown in figure 6.15. The experiments are carried out continuously, but are only shown in figure 6.15 at the indicates times. At first, the catalyst is pre-conditioned by performing the standard experiment continuously for 120 minutes. This should remove most of the sub-surface oxygen. After these 120 minutes, the steady-state mixture is fed and the first measurement is carried out with the quadrupole mass spectrometer. After 30 minutes of feeding the steady-state mixture (t = 150 min.) this experiment is repeated. Both results, in the form of the CO₂ production, are shown in section 1 of figure 6.15. The activity of the catalyst decreased after the switch from transient to steady-state experiments, and even more 30 min. later. At t = 155 min., transient experiments are started again, and their results are shown at t = 155 min., at 165 min., and at 205 min. As can be seen in section 2 of figure 6.14, the initial activity is rather low, but increases in time.

This procedure is repeated in sections 3 (again steady-state, t = 210 and 240 min.) and by section 4 (again transient, t = 255 and 260 and 285 min.) in order to illustrate the reversibility of the process: the steady-state experiments show an initial high activity, which decreases in time, while the transient experiments show that the initially low activity can be restored.

After the experiments in section 4 (figure 6.15), a new type of transient experiments was performed. One feed contained 0.30 kPa C₂H₄ and 0.45 kPa O₂ (i.e. a rich mixture), and the other feed contained 0.07 kPa C₂H₄ and 0.55 kPa O₂ (i.e. a lean mixture). These feeds were alternated over the reactor at a frequency of 1/6 Hz. The results are shown in section 5 for time-on-stream 300 and 360 min., and they indicate a decrease in activity. It shows that, according to the presented theory, the presence of oxygen for a prolonged period of time is required for deactivation to occur. Finally, section 6 shows that the catalyst activity can be fully restored again when the standard experiment is performed again (t = 375 and 415 min.).

The experiments shown in figures 6.13 - 6.15 clearly support the theory of reversible deactivation by over-oxidation of the noble metal surface. They also show that over-oxidation
is not an issue during experiments where one feed containing O\textsubscript{2} is alternated with one feed without no oxygen. During the latter type of experiments the catalyst activity is high and stable. Therefore the experimental results from which the ethylene oxidation kinetics were derived (Chapter 3), do not require model steps to account for this reversible type of deactivation. But the model in its current form is unable to give adequate predictions of experiments as shown in figure 6.12. The model needs extension with additional steps to account for the described phenomenon. Experiments as shown in figure 6.14 may help in determining the rate parameters for the oxidation and reduction steps involved.

![Figure 6.15](image-url)

**Figure 6.15.** Activity of a Pt/Rh/\text{CeO}_2/\gamma-\text{Al}_2\text{O}_3 catalyst, represented by the maximum CO\textsubscript{2} concentration as a function of time-on-stream during subsequent steady-state and transient oxidation of ethylene. 1: two steady-state experiments (0.15 kPa C\textsubscript{2}H\textsubscript{4} and 0.55 kPa O\textsubscript{2} at 423K) performed after 120 and 150 min. of transient experiments at the "standard conditions" (0.15 kPa C\textsubscript{2}H\textsubscript{4} in He alternated with 0.55 kPa O\textsubscript{2} in He at 423 K and 1/6 Hz). 2: standard transient experiments after 155, 165 and 205 min. 3: steady-state experiments after 210 and 240 min. 4: standard transient experiments after 255, 260 and 285 min. 5: transient experiments at 423 K with an amplitude ≠100% (feed1: 0.30 kPa C\textsubscript{2}H\textsubscript{4} and 0.45 kPa O\textsubscript{2} in He; feed2: 0.07 kPa C\textsubscript{2}H\textsubscript{4} and 0.55 kPa O\textsubscript{2} in He) after 300 and 360 min. 6: standard transient experiments after 375 and 415 min. Sections (1-6) represents approximately 50 s of experimentation time, and the experimental conditions are not changed within each section.

The results of figure 6.15 do not support the theory of noble metal segregation as an explanation for the observed differences in catalyst activity. This is because Beck et al. (1993) mention that the enrichment of Rh after switching from a rich to a lean mixture proceeds in the order of seconds, and the enrichment of Pt after switching from lean to rich proceeds in the order of hours. The data from figure 6.15 indicate that both activation and deactivation processes occur in the order of minutes. This issue could be resolved if the experiments shown in figure 6.15 would be performed on a Pt/\gamma-\text{Al}_2\text{O}_3 catalyst for comparison.

6.5.3. *Simulation of exhaust gas conversion at high oxygen content*

Experiments were done in order to investigate whether the current model can be used for prediction of diesel/lean burn exhaust gas conversion. Diesel/lean burn gases were simulated
by slightly lowering the hydrocarbon and carbon monoxide concentrations, while slightly increasing the nitric oxide concentration, and drastically increasing the oxygen concentration compared to the experiment in section 6.5.2. One feed contains slightly less lean components and slightly more rich components than the other. The conditions used in this experiment are listed in table 6.7. For experimental reasons, sulphur dioxide and soot were not added. Diesel exhaust gases always contain small amounts of soot and sulphur dioxide. Soot may accumulate in the catalyst, leading to possible blocking of channels. Sulphur dioxide causes catalyst deactivation and inhibition of the three-way reactions. In the used experimental set-up no facilities to add soot and sulphur dioxide are present. Furthermore, soot and sulphur dioxide may be harmful for the analysis equipment. A frequency of 1/10 Hz was chosen to invoke transient behaviour. Figure 6.16 shows the results of the experiment at 498 K, together with the model predictions. The model predicts a light-off for carbon monoxide, resulting in a very high CO₂ concentration and a very low CO concentration. In the experiment, the CO conversion is much lower. This is probably due to the same phenomenon as was discussed in section 6.5.2.: over-oxidation of noble metal leading to catalyst deactivation due to the continuous presence of O₂. The extremely high concentration of O₂ might cause an even higher deactivation than in the previously described experiment. At lower temperatures than 498 K, hardly any CO₂ was found. At higher temperatures catalyst ignition occurred. It is clear that high concentrations of oxygen are beneficial for an early light-off during the cold start period, as light-off takes place at approximately 100 K lower temperature, in comparison to a stoichiometric feed. Again, the reason that especially the CO conversion is predicted to be high, may be the fact that the oxidation of CO is the fastest reaction in the model.

The measured time averaged fractional conversions are presented in table 6.7. The conversions are lower than in the former experiment, due to the lower temperature, but the trends are similar. Apart from the CO₂ and CO concentrations, the other concentrations are reasonably well predicted. The high oxygen concentration causes a low NO conversion, as is to be expected. Some adsorption and desorption of NO is observed, and some NO is converted to NO₂. This latter reaction is the main cause of the NO conversion, as also predicted by the model. The experiment has been simulated using the following capacities: \( L_T = 1.3 \times 10^{-2} \text{ mol/kg} \), \( L_{\text{INT}} = 6.0 \times 10^{-3} \text{ mol/kg} \), \( L_M = 1.6 \times 10^{-2} \text{ mol/kg} \), and \( \theta_{\text{CH}_x} = 0.69 \).

### Table 6.7

Reactor inlet concentrations during the 1/10 Hz switching experiments between two lean feeds, in order to simulate diesel exhaust gases in the absence of soot, sulphur dioxide, water and carbon dioxide.

<table>
<thead>
<tr>
<th></th>
<th>feed 1</th>
<th>feed 2</th>
<th>conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_2\text{H}_4 )</td>
<td>1550 ppm</td>
<td>1000 ppm</td>
<td>7 %</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_2 )</td>
<td>850 ppm</td>
<td>500 ppm</td>
<td>13 %</td>
</tr>
<tr>
<td>CO</td>
<td>0.53 vol. %</td>
<td>0.33 vol. %</td>
<td>9 %</td>
</tr>
<tr>
<td>NO</td>
<td>0.11 vol. %</td>
<td>0.20 vol. %</td>
<td>7 %</td>
</tr>
<tr>
<td>O₂</td>
<td>4.2 vol. %</td>
<td>5.0 vol. %</td>
<td>8 %</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.0 vol. %</td>
<td>0.0 vol. %</td>
<td>-</td>
</tr>
<tr>
<td>H₂O</td>
<td>0.0 vol. %</td>
<td>0.0 vol. %</td>
<td>-</td>
</tr>
</tbody>
</table>

\( \lambda \)\hspace{1cm}3.74\hspace{1cm}6.97

According to the model, the noble metal surface is approximately covered for 70 % by \( \text{C}_2\text{H}_2 \), 19 % by \( \text{NO}_2 \), and 9 % by NO. The ceria surface contains mainly oxygen (91 %), while the ceria sub-surface layer contains a large amount of \( \text{NO}_2 \) (91 %).
The general conclusion about the applicability of the model for the prediction of diesel/lean burn experiments is similar to the conclusion about the 1 Hz experiment described in section 6.5.2. Light-off of CO is predicted to occur at a lower temperature than was seen in the experiment. The formation of an inactive sub-surface oxygen may be the cause of the low activity during the experiment, which the model does not account for.

![Figure 6.16. Reactor outlet concentrations (markers, measurements; lines, model predictions) versus time for the oxidation of C\(_2\)H\(_2\), C\(_2\)H\(_4\) and CO by NO and O\(_2\) at a temperature of 498 K and an oscillation frequency of 1/10 Hz under lean conditions as mentioned in Table 6.7. A shows the O\(_2\), CO and CO\(_2\) concentrations; the O\(_2\) concentration is depicted on the right axis. B shows the C\(_2\)H\(_4\), C\(_2\)H\(_2\), NO and NO\(_2\) concentrations. The concentrations of N\(_2\) and N\(_2\)O are too small to visualise.](image)

6.5.4. Engine bench tests

This section discusses engine bench tests, performed at dmc\(^2\) (Hanau, Germany). In these tests the exhaust gas of a 1.9L BMW gasoline engine was fed to a monolith (15x10 cm), onto which the catalyst powder has been coated. More details about the conditions and used reactor are described in section 6.2. The experimental results indicate the model's ability to predict real life exhaust gases. Next to the presence of large concentrations of water and carbon dioxide, also small concentrations of sulphur dioxide and a wide variety of hydrocarbons, other than the model components as used in this thesis, will have an influence on the catalyst performance. Also it is likely that oxygen is present during the entire experiment. Furthermore, at high temperatures, reactions not included into the model may become important, such as steam reforming and the water-gas-shift reaction. Two types of tests have been performed: light-off tests, where the catalyst temperature is increased in about
13 minutes from 484 to 709 K at stoichiometric ($\lambda = 1$) and slightly lean ($\lambda = 1.15$) conditions, and a $\lambda$-sweep test, performed at one single catalyst inlet temperature of 673 K. During the latter experiment, the $\lambda$ value is changed from 0.99 to 1.03 and back in 8 minutes at 673 K, i.e. after catalyst light-off.

Figure 6.17 shows the measured temperature at the outlet of the monolith reactor versus time. Figures 6.18 and 6.19 show the results of the stoichiometric ($\lambda = 1$) and the lean ($\lambda = 1.15$) light-off experiment. The markers represent the measurement and the drawn lines show the model calculations.

For the monolith calculations, the rate parameters for the desorption of OCO* as carbon dioxide (step 6f, table 6.4) has been changed to $A = 2.52 \times 10^7$ s$^{-1}$ and $E = 59$ kJ/mol, in order to avoid noble metal surfaces fully covered with OCO* at high temperatures. The values of the rate parameters for the formation and decomposition of OCO* have been determined in the temperature range 393 - 433 K. Using these values at temperatures below 600 K, as was done in this thesis up to this section 6.5.4., did not yield any problems in predicting the experiments adequately. At higher temperatures, however, OCO* according to the model starts to accumulate on the noble metal surface, blocking almost all sites for reactions, and making the catalyst rather inactive. Experiments do not confirm this point, meaning that rate parameters for the formation and decomposition of OCO* may not be extrapolated beyond 600 K. Since the adsorption rate parameter is rather temperature independent, the reaction rate of OCO* to gaseous CO$_2$ had been modified for the engine-bench experiments, in such a way that OCO* does no longer inhibit at high temperatures, while the values of the rate coefficients at temperatures near 400 K are affected as little as possible.

The concentration of hydrocarbons depicted on the right axis, is modelled assuming 70% ethylene and 30% acetylene. The concentration of C$_2$H$_2$ is similar to the concentrations expected in a real exhaust gas (see Chapter 4). Although ethylene is assumed to be a good representative for most hydrocarbons in an exhaust gas, this assumption may not hold for alkanes in particular, which adsorb much slower onto the catalyst surface than ethylene does. NO stands for the sum of the NO and NO$_2$ concentration, and HC stands for the sum of all hydrocarbon concentrations (in case of the measurement) or the sum of ethylene and acetylene concentrations (in case of the calculation). A coverage with carbonaceous deposits of 10% was assumed. It is expected that at high temperatures the carbonaceous deposits will be burned off, and therefore the coverage has been set to a quite low value. In reality, the fraction of carbonaceous deposits may vary with temperature. Using a fraction of carbonaceous deposits of 30%, the description of the stoichiometric light-off test becomes slightly worse, but the prediction of the lean light-off test becomes slightly better. The differences, however, are not large.

The stoichiometric light-off test (figure 6.18) is better predicted than the lean light-off test (figure 6.19). The light-off times during the stoichiometric light-off test are all adequately predicted by the model. Light-off times for the lean test are well predicted as well, but the predicted rates of light-off are too slow compared to the experiment, and the conversion of NO is somewhat overestimated.
Figure 6.17. Reactor outlet temperature versus time for the engine-bench light-off test.

Figure 6.18. Results of the stoichiometric light-off engine-bench test ($\lambda = 1$). The markers represent the measurements and the drawn curves show the model calculations. The hydrocarbon concentrations (HC) are depicted on the right y-axis.

Figure 6.19. Results of the lean light-off engine-bench test ($\lambda = 1.15$). The markers represent the measurements and the drawn curves show the model calculations. The hydrocarbon concentrations (HC) are depicted on the right y-axis.

The lean reactor feed causes the conversion of NO to be very low after the catalyst light-off, because the catalyst surface will be highly covered by oxygen as soon as all rich components have been converted. Apparently, the model predicts some conversion of NO after the light-off in the front part of the monolith, where still rich components are available. This also could be due to the too slow conversion of the hydrocarbons predicted by the model, as can be seen
from figure 6.19. As long as hydrocarbons are present in the exhaust gas, NO can be converted. Possibly, the concentration of acetylene from the engine during the lean test was less than during stoichiometric conditions. That would cause the light-off to occur faster. Also, the presence of steam during the experiment is a reason for the faster light-off than predicted by the model. It was found in section 6.4 that the combination of steam and oxygen very strongly enhance the rates of the bifunctional path reactions. Finally, water-gas-shift and steam reforming reactions, which are not included into the model, can have an effect on the rates of light-off during the experimental conditions.

It is not clear what the influence of a possible over-oxidation of the noble metal may have on the light-off tests. The rate enhancing effect of water and the catalyst deactivating effect of over-oxidation may have more or less cancelled each other during the stoichiometric test, while during the lean test the influence of water is stronger than the over-oxidation. Also, it is not known how both effects change with temperature, and whether they affect each other. More experiments are required in order to reach a conclusion.

Figure 6.20 shows the monolith inlet \( \lambda \) value as a function of time during the \( \lambda \) sweep test. The inlet \( \lambda \) value oscillates around \( \lambda = 1.01 \) with a period of approximately 500 s and an amplitude of 0.02. Figure 6.21 shows the measured and model predicted outlet concentrations versus time at 673 K, corresponding to the inlet data shown in figure 6.20.

At the temperature of this experiment, i.e. 673 K, the catalyst light-off has been reached, but deviations from \( \lambda = 1 \) cause incomplete conversions. During the rich half-cycle NO and O\(_2\) (O\(_2\) is not shown, because it was not measured behind the catalyst) are fully converted, but HC and CO are not, while during the lean half-cycle the situation is reversed. Only during a short time before and after \( \lambda = 1 \) is passed, all conversions are 100 %. It can be seen that the model predicts a too low conversion of CO during the rich time and a too high conversion of NO during the lean time, while the conversion of hydrocarbons is reasonably well predicted. The deviations between the model and the measurements are probably the same as were encountered during the lean light-off test. Therefore, they may be explained by the same reasons. Again, especially the presence of water will have a large influence. High concentrations of H\(_2\)O and CO\(_2\) inhibit the adsorption of NO on ceria, and water strongly promotes the conversion of especially CO, as was shown in section 6.4.
6.6. Conclusions

The four separate sub-models for CO, C₂H₄, and C₂H₂ oxidation, and NO reduction have been added to one combined transient model for an exhaust gas reacting over a commercial three-way catalyst. This full model was compared to various experimental tests with both artificial and more realistic exhaust gases. Some rate parameters have been adapted, in order to increase their applicable temperature range. An extra step for the bifunctional path involving ethylene oxidation at temperatures above 500 K has been added. The model is able to give adequate predictions of the transient kinetic experiments with an artificial exhaust gas, where one reactor feed contains the rich components only and the other one contains the lean components.

The influence of high concentrations of carbon dioxide and water in both reactor feeds was investigated by comparing experiments where 10 vol. % water and/or carbon dioxide had been added to both reactor feeds. Carbon dioxide appeared to be able to adsorb reversibly onto the ceria surface, where it inhibits the adsorption of both oxygen and nitric oxide. The influence of water is much more complex. It also adsors reversibly onto the ceria surface, where it inhibits the adsorption of nitric oxide on the one hand, but enhances the availability of oxygen for bifunctional path reactions on the other hand. The experiments show that the rate enhancement of water is extremely large. The underlying mechanism is still unclear, but must involve at least the oxygen atoms of the water molecules. Furthermore, oxygen must be available for the rate enhancement to occur, which together with the relatively low temperatures excludes water-gas-shift reactions.

The model has been verified in a number of experiments, performed at conditions more close to real-life exhaust gas catalysis. Generally, the model predicts too high conversions of carbon monoxide when both oxygen and carbon monoxide are present in both feeds to the reactor. This could indicate that a type of catalyst deactivation takes place, which does not occur during experiments with an amplitude of 100%. A slow reversible over-oxidation of noble metals could be an explanation for this, but noble metal segregation is an option as well. For practical applications, the model should be extended or adapted to account for these more slow processes on the catalyst.
The engine-bench tests show different results. The stoichiometric light-off test is much better predicted than the lean light-off test. The lambda sweeps test shows similar deviations between the model and the measurement as seen in the lean light-off test. These may be due to reactions, which have not been included into the model, such as water-gas-shift, steam reforming and rate enhancement by water.

In general, it can be concluded that the model is able to adequately predict the kinetic experiments, where one feed with rich components is alternated with a feed containing lean components at temperatures equal to or lower than 573 K. The model predictions, regarding experiments more close to realistic conditions and the engine bench tests, can be improved by adding reaction steps to the model, which appear to be important at these experimental conditions. These are especially the reversible over-oxidation of noble metal sites, and the rate enhancing effect of water.

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Appendix A: The monolith reactor model

The monolithic reactor is modelled as a one-dimensional adiabatic reactor, thus ambient heat losses are not considered. All channels are assumed to have equal diameters and the walls of the channels are impenetrable to gas. The radial gas velocity distribution is assumed to be uniform. Under these conditions only one channel can be modelled as representative for the whole converter. Since the Taylor criterion (Taylor, 1953) is satisfied, the laminar flow in the small diameter channel can be approached as plug flow. Constant heat and mass transfer coefficients based on limit values of the Nusselt and Sherwood numbers for laminar flow are used to describe mass and heat transfer from bulk gas to washcoat.

The continuity equation for a reactant i (i = CO, O₂, NO, C₂H₄, C₂H₂, CO₂, H₂O) in the bulk gas phase is given by:

\[
\frac{\partial}{\partial t}\left(\frac{C_{f,i}}{\rho_f}\right) = -\Phi_{m}^{sup} \frac{\partial}{\partial x}\left(\frac{C_{f,i}}{\rho_f}\right) - \rho_f k_{f,i} a_f \left(\frac{C_{f,i}}{\rho_f} - \frac{C_{s,i}}{\rho_f}\right),
\]

(A1)

and in the solid phase by:

\[
\varepsilon_a \rho_f \frac{4ed_{in}}{d_b} \frac{\partial}{\partial t}\left(\frac{C_{s,i}}{\rho_f}\right) = \rho_f k_{f,i} a_v \left(\frac{C_{f,i}}{\rho_f} - \frac{C_{s,i}}{\rho_f}\right) - a_{cat} (r_{a,i} - r_{d,i})
\]

(A2)

The last term in the equation (A2) accounts for the adsorption and desorption of the species to and from the noble metal and oxygen storage surface. The dependent variables are expressed as C/\rho_f to correct for the density changes as a function of the axial co-ordinate due to non-uniform temperatures. The energy equations in the gas and solid phases are given by:

\[
\varepsilon_f c_{pf} \frac{\partial T_{f,j}}{\partial t} = -\Phi_{m}^{sup} c_{pf} \frac{\partial T_f}{\partial x} - \alpha a_{\varepsilon} (T_f - T_s)
\]

(A3)

\[
(1 - \varepsilon) c_{ps} \frac{\partial T}{\partial t} = \lambda_s (1 - \varepsilon) \frac{\partial^2 T}{\partial x^2} + \alpha a_{\varepsilon} (T_f - T_s) + a_{cat} \sum_j (\Delta H_j) r_j
\]

(A4)

The reaction heat generation is accounted for in the last term of equation (A4). It is calculated using the rates of global reactions, r_j. This is allowed since the heat capacity of the reactor is much higher then the heat production due to changing surface coverage (v. Selow, 1996). The continuity equation for the species j adsorbed on the noble metal surface or ceria surface can be written as follows:

\[
L_{CAP} \frac{\partial \theta_j}{\partial t} = r_{a,j} - r_{d,j} + \sum_k r_{k,j}
\]

(A5)

where k denotes a certain surface reaction which involves the species j, and L_{CAP} stands for either L_{OSC} or L_{NM}.

References
Appendix B: Assessment of the sensitivity of the kinetic rate parameters

The values of the rate parameters, obtained in this thesis, have been determined by means of multi-response non linear least squares regression analysis of the experimental data by the model. The errors in the rate parameters are caused by experimental errors, model errors, and regression errors. The magnitude of these errors is normally determined by assessing the confidence intervals for each rate parameter. However, the estimation of the confidence intervals for the rate parameters for transient models is not straight-forward. The classical approach would be to perform the so-called t-test, which determines the relevance of each individual rate parameter. A basic assumption for the use of the t-test is that the noise, i.e. the deviations between the measured data-points and the model-predicted data-points, is randomly distributed around zero and uncorrelated. This means that the residuals (the difference between the values of the measured data-points and the values of the model-predicted data-points) must have a Normal distribution. This is usually the case for experimental noise, since the experimental results contain some error (e.g. noise from mass-flow-controllers, or from the mass spectrometer). If the experiments were repeated several times under the same conditions, and the results would be averaged, this (random) noise would be reduced.

In case of transient modelling, the assumption of random and uncorrelated noise is no longer valid. Since the kinetic model is not perfect, there are systematic deviations between the measurement and the model. These deviations are, therefore, not only due to experimental noise, but are also the result of an incomplete model, the so-called lack-of-fit. In kinetic modelling, this is generally the case, since kinetic models are often kept as simple as possible, even in the case of steady-state modelling. In case of modelling of time-series of data points, this will cause the errors to be systematic: the value of an error of a certain data-point depends on the error of previous data-points in time. Hence the assumption of random and uncorrelated noise cannot hold. This is illustrated by means of two residuals plots from Chapter 4. Figure B.1a shows the residuals of the steady state acetylene oxidation experiments (see section 4.3). Figure B.1b shows the same results in the form of a histogram, where the results have been grouped into sections of 2.5 %. Since every experiment yields only one data-point, all experimental results are independent, i.e. only experimental noise contributes to the errors. It can be seen that indeed the data-points are randomly distributed around zero. Figure B.2 shows the residual plot of the acetylene concentration during the transient acetylene oxidation (see section 4.4, figure 4.5). This figure clearly shows that there are systematic deviations between the model predictions and the experimental data, which are heavily correlated (e.g. at t = 12 s and at t = 22 s). The deviations located between these "peaks", are due to experimental noise. These are not distributed around zero, because the model predicts a zero acetylene concentration, while the mass spectrometer always measures some background signal.

A way to circumvent the unwarranted assumption of the Normal distribution, would be to consider other distributions, which would be valid for the particular case. This approach would however not work in this case, since the distribution changes with time in the same way as the experimental results. Since it is not possible to assume a certain distribution, an assessment of confidence intervals without any statistical distribution would be required. There are possibilities for the assessment of such intervals, but these would exceed largely beyond the scope of this thesis. The method of determining the rate parameters, non-linear least squares regression analysis, is a robust method, but the theory about the confidence intervals has not yet been sufficiently developed, and has not been implemented altogether.
A more practical approach is to investigate the dependence of the individual rate parameters on the weighted sum of squares (SSQ). If the SSQ increases strongly, when a parameter is slightly changed, then this rate parameter has a large sensitivity, and thus a small confidence interval. On the other hand, if the SSQ hardly increases, when changing the value of a rate parameter, then this parameter has a lower sensitivity and thus a larger confidence interval. In this case the sensitivity of an individual rate parameters is defined as the increment of the weighted sum of squares at a given change (either positive or negative) of the rate parameter. So, the fractional increment of a rate parameter, necessary to obtain an increase of the SSQ of e.g. 10%, is a measure for the sensitivity and confidence interval of the parameter. The advantage of this approach is that no assumptions about a statistical noise distribution have to be made. The disadvantage is that no absolute confidence interval is obtained, but only a relative indication of the size of the confidence interval. The approach is similar to a sensitivity analysis. The non-linearity of the total system will require the assessment of both increasing and decreasing the individual rate parameters, since a different result may be obtained.

This is illustrated by two examples, shown in figures B.3 and B.4. Figure B.3 shows the SSQ dependency on the maximum allowed fractional oxygen coverage, due to deposition of carbonaceous matter, and figure B.4 shows the same dependency for the activation energy for combustion of di-σ ethylene. The curves have been determined by calculating the SSQ while...
changing the rate parameters by multiplication of the optimal value with various factors, leaving all other parameters at their optimal values. It is assumed in this approach, that the values of the different rate parameters are uncorrelated. This assumption may not hold for all parameters, but is required in order to perform this exercise. As can be seen, the curve in figure B.3 is more or less symmetrical, indicating that the parameter is equally sensitive for augmentation as for reduction. The curve in figure B.4 shows that a reduction of the parameter would largely increase the SSQ, while increasing the parameters hardly changes the SSQ. This means that for the fit, the value of the parameter is not essential, as long as its value supersedes a certain value. Since the rate parameter is an activation energy, this means that the rate coefficient of this step may not become fast. A maximum rate parameter is indicated, but a minimum cannot be determined. This may indicate that this step does not contribute much to the overall model prediction. From a chemical point of view, it was already considered in Chapter 3 that the combustion of di-\(\sigma\) ethylene is quite slow. Especially at temperatures higher than 500 K, this step may become important.

Finally, figure B.5 illustrates that also non-trivial dependencies of rate parameters on the SSQ can occur. Fortunately, the behaviour around the minimum is quite symmetrical, so there is no problem in determining the values for the parameter for which the SSQ is increased by 10\%. However, further away from the optimal parameter value, the SSQ dependency on the parameter value shows a different behaviour, such as different slopes and even a local minimum. This illustrates why a SSQ increase of 10\% is used for comparing the relevance of the individual rate parameters; the use of higher percentages may lead to ambiguous results.

As far as possible, the upper and lower values of the rate parameters obtained by regression in Chapters 3, 4, and 5, corresponding with a 10 \% SSQ increase, have been determined. In some cases, one or both values could not be determined (e.g. the case shown in figure B.4). This indicates that a parameter is not very sensitive. The results are shown in Tables B.1 (ethylene oxidation), B.2 (acetylene oxidation) and B.3 (NO reduction). These values are shown as a percentage of the optimum rate parameter, hence a low percentage corresponds with a small confidence interval, while a large percentage corresponds with a large interval. As mentioned before, the numbers do not give an absolute judgement about the relevance of the rate parameters, but only provide a relative indication.

Generally, the values of the activation energies are more accurately predicted than the values of the pre-exponential factors. This is probably caused by the exponential function of the
Arrhenius plot. A small deviation in the exponent will cause a larger difference than a small deviation in the pre-exponential factor.

**Figure B.3.** The sum of squares versus the value of the maximum allowed oxygen coverage due to carbonaceous deposits during the transient acetylene oxidation (Chapter 4, section 4.4). The vertical dotted lines indicate the parameter values corresponding with a sum of squares 10% higher than the optimal one.

**Figure B.4.** The sum of squares versus the value of the activation energy for the combustion of di-σ ethylene (Chapter 3, section 3.5). The parameter values corresponding with a sum of squares 10% higher than the optimal one on the lower side is indicated with a dotted line. The upper value cannot be determined from this plot.

**Figure B.5.** The sum of squares versus the value of the activation energy for the desorption of acetylene (Chapter 4, section 4.4). The vertical dotted lines indicate the parameter values corresponding with a sum of squares 10% higher than the optimal one.

In case of the ethylene oxidation, especially the rate parameters of steps 3f and b are predicted quite accurately. These steps represent the reversible transition from π ethylene to di-σ ethylene. It was shown in Chapter 3 that these steps cause the typical shape of the carbon dioxide peaks, so it can be understood that these steps are quite critical. On the other hand it was expected that the Eley-Rideal type path, where ethylene can adsorb onto an oxygen covered site, is only an initiation step, to allow ethylene to react when a lot of oxygen is
present on the noble metal surface. The corresponding rate parameters of steps, 6f and 7f, indeed are estimated with less accuracy than the values of most other steps. The same holds for the oxidation step of di-σ ethylene (step 4f).

Table B.1. Estimates of the kinetic rate parameters for the transient ethylene oxidation by oxygen over Pt/Rh/CeO2/γ-Al2O3 from Chapter 3, Table 3.3. The parameters with ” are taken from Nibbelke et al. (1998a). The parameters with # are set to low values for numerical stability only (Nibbelke et al., 1998b). Units k: m3/mol/s, A: s-1, E: kJ/mol.

The lower % and upper % indicate the fractional decrease respectively increase of the rate parameter, necessary to increase the weighted sum of squares by 10%. "n/a" indicates that the parameter was not obtained via regression in this work. "-" indicates that the 10% increase was not reached within the investigated range. Values above 100% have been determined by extrapolation of the SSQ.

<table>
<thead>
<tr>
<th>parameter value</th>
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<th>upper %</th>
</tr>
</thead>
<tbody>
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<td>n/a</td>
<td>A4</td>
<td>1.06 10^10</td>
<td>-</td>
</tr>
<tr>
<td>k1</td>
<td>1.00 10^10</td>
<td>n/a</td>
<td>E4</td>
<td>254</td>
<td>1.1 %</td>
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<tr>
<td>k2</td>
<td>1.26 10^6</td>
<td>48.6 %</td>
<td>A5</td>
<td>3.55 10^2</td>
<td>6.0 %</td>
</tr>
<tr>
<td>A</td>
<td>3.33 10^9</td>
<td>15.8 %</td>
<td>E5</td>
<td>11.3</td>
<td>5.9 %</td>
</tr>
<tr>
<td>E</td>
<td>75.5</td>
<td>2.3 %</td>
<td>k6</td>
<td>14.7</td>
<td>-</td>
</tr>
<tr>
<td>A</td>
<td>1.39 10^6</td>
<td>5.0 %</td>
<td>6.0 10^3</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>E</td>
<td>76.8</td>
<td>0.06 %</td>
<td>A7</td>
<td>1.52 10^10</td>
<td>83.6 %</td>
</tr>
<tr>
<td>A</td>
<td>5.39 10^4</td>
<td>1.1 %</td>
<td>34.2 %</td>
<td>E7</td>
<td>78.7 10^4</td>
</tr>
<tr>
<td>E</td>
<td>23.0</td>
<td>3.6 %</td>
<td>2.0 %</td>
<td>θ</td>
<td>0.66</td>
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</table>

In case of the transient acetylene oxidation, the values of the parameters for the desorption rate of acetylene (step 1b) is predicted quite accurately, compared with other rate parameters. The desorption rate does not only control the acetylene concentration, but also the rate of adsorption of oxygen; in case of a too slow desorption rate for acetylene, an oxygen breakthrough peak would be predicted, while none was measured, which would lead to a large increase in the SSQ. The values of steps 5b and 6f cannot be predicted very accurately compared with other rate parameters. Both steps involve the Eley-Rideal path for acetylene, which was shown to be very important for acetylene oxidation. It was mentioned in Chapter 4 that the C2H2O× species was expected to be very unstable, which indicates that its disappearance rates would be quite high. This would indeed cause the values of the corresponding rate parameters to become difficult to quantify accurately. The formation of this species, which then controls to total rate for this path can be estimated more accurately.

Table B.2. Estimates of the kinetic rate parameters for the acetylene oxidation by oxygen over Pt/Rh/CeO2/γ-Al2O3 from Chapter 4, Table 4.6. The lower % and upper % indicate the fractional decrease respectively increase of the rate parameter, necessary to increase the weighted sum of squares by 10%. "n/a" indicates that the parameter was not obtained via regression in this work. "-" indicates that the 10% increase was not reached within the investigated range. Values above 100% have been determined by extrapolation of the SSQ. Units k: m3/mol/s, A: s-1, E: kJ/mol.

<table>
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</tr>
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<td>5.34 10^2</td>
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<td>318.0 %</td>
<td>k6</td>
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<td>A7</td>
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<tr>
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<td>-</td>
<td>-</td>
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<td>124</td>
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<td>11.0 %</td>
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</table>
Table B.3. Estimates of the kinetic rate parameters for the nitric oxide reduction by carbon monoxide from Chapter 5, Table 5.3. Units k: m$^3$/mol/s, A: s$^{-1}$, E: kJ/mol, L: mol sites kg$^{-1}$. The lower % and upper % indicate the fractional decrease respectively increase of the rate parameter, necessary to increase the weighted sum of squares by 10%. "n/a" indicates that the parameter was not obtained via regression in this work. "-" indicates that the 10% increase was not reached within the investigated range. Values above 100% have been determined by extrapolation of the SSQ.

<table>
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<td>$k_{30}$</td>
<td>5.34 10$^b$</td>
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<td>-</td>
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<tr>
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<td>59.5%</td>
<td>-</td>
<td>$A_{21}$</td>
<td>1.03 10$^{17}$</td>
<td>75.8%</td>
<td>-</td>
</tr>
<tr>
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<td>6.4%</td>
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<td>2.6%</td>
</tr>
<tr>
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<td>68.3%</td>
<td>135%</td>
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<td>7.78 10$^{18}$</td>
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</tr>
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<td>1.6%</td>
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<td>10.0%</td>
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<td>89.6%</td>
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<td>80.9%</td>
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<tr>
<td>$A_{15}$</td>
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<td>80.1%</td>
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<td>17.3%</td>
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<tr>
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</tr>
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<td>-</td>
<td>-</td>
<td>$E_{24}$</td>
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<td>10.7%</td>
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<tr>
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<td>-</td>
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<td>$E_{17}$</td>
<td>20.1</td>
<td>36.7%</td>
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<td>$A_{25}$</td>
<td>2.45 10$^5$</td>
<td>81.0%</td>
<td>145%</td>
</tr>
<tr>
<td>$A_{18}$</td>
<td>4.08 10$^f$</td>
<td>92.6%</td>
<td>-</td>
<td>$E_{25}$</td>
<td>22.4</td>
<td>20.2%</td>
<td>34.7%</td>
</tr>
<tr>
<td>$E_{18}$</td>
<td>56.6</td>
<td>24.9%</td>
<td>17.6%</td>
<td>$A_{25b}$</td>
<td>6.60 10$^8$</td>
<td>63.7%</td>
<td>-</td>
</tr>
<tr>
<td>$k_{19}$</td>
<td>5.85 10$^f$</td>
<td>57.8%</td>
<td>91.6%</td>
<td>$E_{25b}$</td>
<td>65.6</td>
<td>12.1%</td>
<td>7.0%</td>
</tr>
<tr>
<td>$A_{19}$</td>
<td>2.27 10$^f$</td>
<td>34.9%</td>
<td>131%</td>
<td>$L_{NN}$</td>
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<td>7.5%</td>
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<td>n/a</td>
</tr>
<tr>
<td>$A_{20}$</td>
<td>2.18 10$^f$</td>
<td>-</td>
<td>-</td>
<td>$A_{CeB}$</td>
<td>1.96</td>
<td>38.9%</td>
<td>63.0%</td>
</tr>
<tr>
<td>$E_{20}$</td>
<td>97.8</td>
<td>5.6%</td>
<td>-</td>
<td>$E_{CeB}$</td>
<td>18.1</td>
<td>11.4%</td>
<td>12.4%</td>
</tr>
</tbody>
</table>

During the NO reduction experiments, it was not possible to calibrate the mass spectrometer for N$_2$O (steps 15 – 17) and NO$_2$ (steps 20), so it is expected that the rate parameters for these steps are predicted less accurately than most other parameters. Indeed the table confirms this expectation. Especially the step for NO$_2$ formation via the Eley-Rideal type path (steps 19) can be estimated quite accurately. This path was a major inhibitor for the CO oxidation, since it was able to shield oxygen adatoms from reaction with adsorbed CO. Also adsorption and desorption of NO on the noble metal are critical steps (steps 13).

It can be concluded that the presented approach is able to give a relative sensitivity for each individual rate parameter. For the presented examples, the global values needed to raise the SSQ by 10% can be understood from the interpretations presented in Chapters 3 – 5.
7

CONCLUSIONS & OUTLOOK

7.1. Conclusions

Introduction
After approximately 25 years of research and development, automotive exhaust gas catalysis is still an important topic. This is caused by the continuous expansion of road traffic leading to an increased severeness of legislation. Catalyst and car manufacturers are continuously forced to improve their products. From a scientific point of view, automotive exhaust gas catalysis is interesting because of the large diversity of chemical and physical processes taking place simultaneously, which may have a profound influence on each other. Many of the related phenomena are not yet fully understood.

The problem of the harmful emissions after the cold start of a car as a result of too slow kinetics at low catalyst temperature, as investigated in this thesis, is just one of the many challenges involved in automotive exhaust gas catalysis. In literature, many mechanistic and catalyst characterisation studies were published while only few kinetic studies on the basis of elementary reaction steps can be found. In most cases, however, these studies mainly focus on one single reaction, involved in automotive exhaust gas conversion, or are performed using model catalysts. Studies on commercial catalysts, while using full exhaust gases, are rather limited to empirical or semi-empirical modelling. Steady-state models, however, have limited use for automotive practice, where steady-state conditions are rarely met. In order to obtain a reliable model which is able to give accurate predictions at real-life automotive conditions, a transient model based on elementary reaction steps is required.

Such a model can be used for the design of a model based engine controller, which allows to optimise the conversion of pollutants. Contrary to the current $\lambda$ sensor based feed-back controllers, which control the inlet $\lambda$ value, a model predictive controller can regulate the degree of oxygen storage of the ceria as one of the catalyst components, which allows a more direct control of the catalytic processes.
In the transient kinetic model developed in this thesis, the following components have been used: C₂H₄, C₂H₂, CO, NO, and O₂, which are converted into CO₂, H₂O, N₂, N₂O, and NO₂. Ethylene and acetylene have been chosen as representative for the hydrocarbons, emitted by the engine, because of their relatively large concentrations in real exhaust gases and because the profound influence of acetylene on the catalyst light-off. The effects of high concentrations of water and carbon dioxide as well as sulphur dioxide and hydrogen have not been included into the model. The catalyst used is a commercial Pt/Rh/CeO₂/γ-Al₂O₃ catalyst supplied by dmc² (Hanau, Germany).

The approach of the kinetic studies was such that a detailed elementary step mechanism for each global reaction was obtained, which lead to an adequate description of kinetic experiments, performed at conditions closely to real-life exhaust catalysis. This is contrary to most studies on automotive exhaust gas kinetics, which either provide an elementary step model, based on experiments under UHV conditions, but not suitable for predictions of real-life converter measurements, or which provide empirical models which cannot be extrapolated outside their range of experimental conditions.

The kinetics for the transient carbon monoxide oxidation over the same Pt/Rh/CeO₂/γ-Al₂O₃ catalyst have been taken from Nibbelke et al. (1998). This thesis focuses first on the additions of ethylene oxidation, acetylene oxidation, and nitric oxide reduction to this model. Thereafter, all sub-models are combined into the full kinetic model, which is then verified via a number of experiments at conditions more close to real-life automotive exhaust gas catalysis.

**Experimental set-up**

The experimental set-up provides means for obtaining transient kinetics of fast reactions, involving isobaric masses. It allows alterations of two gas mixtures with different compositions over a catalytic fixed bed reactor at switching frequencies up to 10 Hz. Isothermal experiments under plug flow conditions can be performed without significant pressure changes after the switches.

A JEOL magnetic sector mass spectrometer was adapted to monitor changes in gas phase concentrations with a sampling frequency of 48 Hz at a mass resolution of 5000 (at 20% cut). This apparatus provides adequately data to monitor 1 Hz oscillations in automotive practice, and the available mass resolution is sufficient to separate CO and N₂ at concentration ratios up to 1:120. N₂O and CO₂ are separately measured as well. The sensitivity is high enough to measure concentrations as low as 0.005 vol. % or lower. The stability is high enough to follow in real time one mass for at least 5 minutes. The signal/noise ratio is sufficiently high in order to distinguish catalytic phenomena from apparatus noise.

**The oxidation of ethylene**

The transient oxidation of ethylene by oxygen was studied via cycling of the feed over the Pt/Rh/CeO₂/γ-Al₂O₃ catalyst. Experiments, under conditions representing the cold start of an Otto motor, indicate the presence of two types of adsorbed species, which are ascribed to π- and di-σ ethylene. The former species can be oxidised rapidly, while the latter is rather refractory. No intermediate products were detected. The presence of ceria does not influence the ethylene oxidation at the investigated conditions.
A kinetic model, based on elementary steps has been proposed, which is able to predict adequately the experimental data for both rich and lean half cycles with one set of rate parameters. An assumption was made about deposition of carbonaceous species on noble metal, leading to selective deactivation of the catalyst. Experimental indications for this phenomenon have been found: elemental analysis showed a high carbon content, and a large difference between the surface capacities of ethylene and oxygen was found.

Extension of the proposed model with the transient model for CO oxidation adequately describes the experimental data of combined ethylene and carbon monoxide oxidation. Carbon monoxide inhibits the conversion of ethylene and is oxidised in the front part of the reactor. The region for ethylene combustion is located at the end of the reactor. Cycling of the feed induces spatio temporal patterns in the reactor.

LEIS analysis shows a Pt surface concentration of about 0.098% of a monolayer in a fresh commercial three-way catalyst. After use in either acetylene or ethylene oxidation at cold start conditions, a decrease of 50±5% of the Pt surface concentration is observed with LEIS. The Pt surface concentration can be completely restored by exposing the used catalyst to atomic oxygen and a subsequent reduction at 573 K. Therefore, the observed Pt loss is not due to sintering, but due to deposition of carbonaceous species during the hydrocarbon oxidation. The observed loss in Pt surface area with LEIS agrees quantitatively with the noble metal area loss as found in kinetic modelling of acetylene and ethylene oxidation, being 60±10% and 40±10%, respectively. Hence, this study shows that LEIS can be successfully applied to quantitatively investigate coke formation on commercial supported three-way catalysts.

**The oxidation of acetylene**

The steady state oxidation of acetylene with oxygen has been investigated at cold-start conditions. The reason to study the steady state conditions was the absence of kinetic data on acetylene oxidation in the literature. It was found that the partial reaction order is negative for acetylene and positive for oxygen. Increasing the temperature led to a higher conversion of acetylene and a lower selectivity to CO. Carbon monoxide was found to be the only primary reaction product, which may be oxidised to CO$_2$ consecutively. A kinetic model for the partial oxidation of acetylene to carbon monoxide has been developed, which was added to the transient kinetics for CO oxidation over the same catalyst. The combined model is able to predict the experimental results quite adequately. The adsorption rate coefficient for acetylene was derived from literature, while a low rate of acetylene desorption was used. Rate parameters for the direct conversion of acetylene to adsorbed carbon monoxide by oxygen on both noble metal and ceria have been obtained by regression.

The transient oxidation of acetylene over a three-way catalyst has been studied for automotive cold start conditions. Feed cycling experiments with oxygen and acetylene indicate the presence of two different acetylene surface species, which were ascribed to reactive π acetylene and refractory di-σ+μ acetylene. Carbon monoxide was found as an intermediate product of the oxidation process. The presence of ceria in the catalyst has a strong effect on acetylene oxidation, which was found to be a direct bifunctional reaction between acetylene adsorbed on the noble metal and oxygen from ceria.

A transient kinetic model for the partial oxidation of acetylene to carbon monoxide was constructed on the basis of the experimental results and literature data. This model was combined with the same model for the transient carbon monoxide oxidation as used in the
steady state study. This combined model is able to describe quantitatively the transient oxidation of acetylene as well as the simultaneous acetylene and carbon monoxide oxidation. An assumption for a selective deactivation through deposition of carbonaceous deposits onto the catalyst had to be made in a similar way as for the ethylene oxidation, in order to describe adequately measured CO$_2$ responses. It was concluded that the presence of gaseous carbon monoxide hardly influences the oxidation of acetylene. On the other hand, the oxidation of carbon monoxide is almost completely inhibited by acetylene, except for the path leading to OCO species on the surface. Furthermore, carbon monoxide and acetylene are both oxidised, by oxygen adatoms from the previous half-cycle, in the same reaction front, which moves through the reactor after the switch from lean to rich conditions. Before this front, the oxidation reactions proceed with oxygen from ceria.

The reduction of NO

Various constituents of the Pt/Rh/CeO$_2$/γ-Al$_2$O$_3$ catalyst have been studied separately with respect to the transient reduction of NO by CO in the presence and absence of oxygen. This comparison of several model catalyst formulations is a successful approach for understanding complex catalyst behaviour. The transient experiments provided new mechanistic insights: reversible adsorption of NO on ceria appeared independent of the oxidation state of ceria; indications of bulk diffusion of NO into ceria; pure ceria cannot dissociate NO, but can store O atoms from NO dissociating on the noble metal.

Chemisorbed CO does not directly react with chemisorbed NO, but leads to additional desorption of NO through cross-desorption. N$_2$ and N$_2$O formation only occur after NO dissociation, which is inhibited by the presence of oxygen. The reduction of gaseous N$_2$O proceeds slower than the reduction of NO, because of slow N$_2$O adsorption. The presence of Rh in the catalyst accelerates the rates of certain reaction steps, but does not alter the mechanism.

The kinetic model is able to predict adequately the experimental data for both rich and lean half cycles with one set of rate parameters. The catalyst has a very large storage capacity for NO, however the presence of oxygen strongly inhibits the dissociation of NO, which is necessary for N$_2$ formation. Both NO and O are stored on the catalyst during the lean half-cycle and released or reduced during the rich part. NO$_2$ formation on the catalyst inhibits the CO oxidation as well as the NO reduction. At the relatively high temperatures used here, effects as sub-surface ceria oxidation and reduction by both NO and O would appear to become important.

The complete model

The four separate sub-models for CO, C$_2$H$_4$ and C$_2$H$_2$ oxidation and the reduction of NO have been combined into one transient model for an exhaust gas reacting over a commercial three-way catalyst. Some rate parameters have been adapted, in order to increase their useful temperature range. As a result of this, the oxidation of carbon monoxide around 400 K is less adequately predicted. The spill-over of carbon monoxide from the noble metal to the ceria surface has been removed from the model, and an additional bifunctional dissociation for NO has been added. An extra step for the bifunctional path involving ethylene oxidation at temperatures above 500 K has been added. The model is able to give accurate predictions of the transient kinetic experiments, where one reactor feed contains rich components and the other contains lean components.
The influence of high concentrations of carbon dioxide and water of both reactor feeds was investigated by comparing experiments where 10 vol. % water and/or carbon dioxide were added to each reactor feed. Carbon dioxide appeared to adsorb reversibly onto the ceria surface, where it inhibits the adsorption of both oxygen and nitric oxide. The influence of water is much more complex. It adsorbs reversibly onto the ceria surface, where it inhibits the adsorption of nitric oxide on the one hand, but enhances the availability of oxygen for bifunctional path reactions on the other hand. The experiments show that the rate enhancement is extremely large (over a factor ten higher). The underlying mechanism is still unclear, but it must involve at least the oxygen atoms of the water molecules. Furthermore, oxygen must be available for the rate enhancement to occur, which excludes the water-gas-shift reaction. The latter is moreover underlined by the relatively low temperatures.

The model has been verified in a number of experiments performed at conditions more close to real-life exhaust gas catalysis. Generally, the model predicts too high conversions of carbon monoxide when both oxygen and carbon monoxide are present in both feeds to the reactor. This could indicate that a type of catalyst deactivation takes place, which does not take place during the experiments where the amplitude equals 100%. The slow reversible over-oxidation of the noble metals in the catalyst could be an explanation for this. Also Rh segregation within the mixed Pt/Rh clusters could be a possible explanation for this effect. For practical applications, the model should be extended or adapted to account for these more slow processes on the catalyst.

Engine-bench tests have been performed in order to investigate whether the model is able to adequately predict real exhaust gas conversion. Light-off tests (stoichiometric and lean) as well as a sweep test have been performed with a monolithic reactor, coated with the same catalyst as was used for kinetic modelling. The stoichiometric light-off test is much more adequately predicted than the lean light-off test. The sweep test shows similar deviations between the model and the measurement as seen in the lean light-off test. The light-off times are adequately predicted but the predicted rates of light-off of CO, HC and NO are too slow. Predicted conversions during the sweep test are too low. Also, too much NO conversion is predicted after the light-off. The reason may be that some reactions, such as water-gas-shift, steam reforming and rate enhancement by water, have not been included into the model become important at high temperatures (> 600 K).

In general, it can be concluded that the model is able to accurately predict the kinetic experiments, where one feed containing rich species is alternated with a feed containing lean components at temperatures equal to or lower than 573 K. The model predictions of the experiments more close to realistic conditions and the engine bench tests can be improved by adding reactions to the model, which appear to be important at these experimental conditions.

7.2. Outlook

The results of this study on the kinetics of automotive exhaust gas reactions are put in a perspective for future research work.

A direct experimental verification of the model predicted fractional surface coverages on the level of elementary steps could be obtained if the fractional surface coverages could be measured in-situ. Available techniques are IR, SIMS, STM and TPD/TPO, but they require conditions which differ greatly from real exhaust gases (Hopstaken & Niemantsverdriet, 2000). Especially the ambient pressure, the extremely short reactor residence time, and the
fast transients make the application of such techniques difficult. Ex-situ measurements also provide very useful information for the modelling or its verification, as was demonstrated by the use of LEIS in chapter 3 and by Jansen et al. (submitted).

Three different themes can be distinguished:
1) model reduction,
2) model extension,
3) model expansion.

1) Model reduction
Current plans for the use of the developed kinetic model include its use in a model predictive controller, as has been mentioned before. The oxygen content of ceria will be continuously optimised during converter operation in order to achieve the highest possible conversions of all components at any prevailing condition (Balenovic et al., 2000). This requires on-board computer calculations of the oxygen storage in the ceria every 10 ms, during which no more then 1-2% of the computers CPU-time should be used. The model in its current form cannot be used for that purpose, because numerically solving the many differential equations requires a large CPU time. Therefore model reduction is required. For the controller model, the measured input variables need to be correlated as simple as possible with the desired output variable. This indeed necessitates a very strong reduction of the model.

In order to reduce CPU times, leaving the kinetic model equations as they are, it may become desirable to reduce the reactor model. This could be achieved by applying less discretisation points in both the reactor and the time co-ordinate. Also, calculations with a lower precision could be performed. These three options lead to lower calculation times, but may introduce errors which could lead to inaccurate or even poor predictions. The approach is most likely successful when steep transients in concentrations and temperatures are absent. Another approach to obtain smaller CPU times could be the removal of certain reaction steps, which may not be needed when only calculations in a limited range of conditions are required. Some steps in the model are only required when the catalytic surface is mainly occupied with one surface species, as will occur often considering the nature of the kinetic experiments used to obtain the model (i.e. 100 % amplitude). Using a sensitivity analysis, the less relevant steps for certain conditions can be identified and removed. This procedure needs an experimental verification in order to ensure that the removal of such steps is indeed justified. The success of this approach is fully dependant on the range of experimental conditions for which the reduced model should work.

A very significant reduction of the calculation time can be obtained if the first-principle model is changed into a black box model (Balenovic et al., 2001). This way the stiff and hard to solve differential equations will be replaced by a number of explicit, algebraic equations. The kinetic rate parameters are replaced by fit parameters without physical meaning. It may be possible to acquire such black box model using a neural net or via an attractor capturing method, on the basis of data generated with the first-principle model. It should be verified that interpolation of the black box model between these data points is accurate.

2) Model extension
Especially the verification experiments, where all components were present in both reactor feeds showed some deviation between the model predictions and the experiments. The predictions of the experiments with component amplitudes of 100% were accurately predicted. For a better application of the model under practical circumstances, the model
could be expanded with steps, which would become important under conditions where, for example, oxygen is always present in the gas phase, such as lean burn conditions. In such case, steps for the slow oxidation of the noble metals could be introduced (Volokitin et al., 1986). Experiments could be performed where amplitudes for oxygen change in time, in order to obtain rate data for these steps. The possible influence of noble metal segregation within Pt/Rh clusters may be verified by comparing the experiments from figure 6.15 with a similar sequence of experiments over a Pt/Al₂O₃ catalyst. If similar results are obtained, then segregation can be excluded as possible explanation for the observed catalyst deactivation.

Another possible extension to the model could concern the influence on kinetics of steam and carbon dioxide. The combustion of the fuel causes high concentrations of H₂O and CO₂ (of the order of 10-14%) in an exhaust gas. The species may adsorb onto the ceria present in the catalyst, inhibiting or enhancing other reactions (Herz, 1981; Padeste et al., 1993). The relatively high concentrations of these components make their influence significant. It has been shown, however, that the influence of especially water is not straight forward, since an increase in the rate of carbon monoxide oxidation and a decrease in the oxidation rate of ethylene has been found (Chapter 6; Nibbelke et al., 1997). The rate enhancement of water is of such a magnitude, that for accurate predictions of engine-bench tests the influence of water should be present in the model. In this respect, also water-gas-shift and steam-reforming reactions can have a significant influence on the conversion of the model components, especially at high temperatures (> 600 K) and under oxygen poor conditions (Whittington et al., 1995).

The presence of hydrogen in exhaust gases could also be introduced into the model. Before the catalyst light-off, hydrogen can be oxidised rather easily. The heat produced by this reaction shortens the light-off period, and is usually accounted for in modelling by adapting the heat of carbon monoxide oxidation (Kuo, 1971). Another issue is that hydrogen will consume some of the available oxygen. At high temperatures, measurements have indicated that the amount of hydrogen in the exhaust gas behind the catalyst can be even larger than in front of the catalyst, indicating that hydrogen is being produced in the converter. This implies that water-gas-shift (CO + H₂O $\rightarrow$ CO₂ + H₂) and steam reforming (CₓHᵧ + H₂O $\rightarrow$ H₂ + CO) reactions have become important (Whittington et al., 1995). For the model to include hydrogen oxidation at low temperature, and water-gas-shift and steam-reforming reactions at high temperature, the following elementary reaction steps could be added, for which the rate coefficients should be determined by regression of transient experiments:

a) H₂ + 2* $\leftrightarrow$ 2H*
b) H* + O* $\leftrightarrow$ OH*
c) OH* + H* $\leftrightarrow$ H₂O*
d) H₂O* $\leftrightarrow$ H₂O + *

Following this scheme from a-d, the oxidation of hydrogen is described, assuming that oxygen is available on the noble metal (or possibly also on ceria). If this scheme is followed in the opposite direction, i.e. d-a, and if the O* being produced in step b were consumed by either carbon monoxide or hydrocarbons, then water-gas-shift or steam reforming would be described. The temperature of the catalyst would then determine which path becomes important. Also, it would be important to investigate the contribution of ceria to such reactions.
3) **Model expansion**

The largest disadvantage of any kinetic model is that it is only valid for the catalyst it has been developed for. Catalysts with different Pt/Rh ratios, with Pd present or with additions of components like ZrO$_2$ will show different kinetics (Bart et al., 1992; Amon-Meziere et al., 1995). The presence of ZrO$_2$ may increase the rates of bi-functional reactions by making the ceria oxygen faster available (Kaspar et al., 1999). In case of (semi-)empirical models a completely new kinetic study is required. For the model, presented in this thesis, most elementary reaction steps are already present, so an accurate description of alternative catalysts can be obtained after a relatively simple re-optimisation of the rate coefficients, if the reaction mechanism remains the same. For the re-optimisation of the rate coefficients, a limited number of transient experiments at several temperatures using the new catalyst is required.

Principally, the model should also be capable of accurately predicting conversions of diesel and lean burn exhaust gases, since the experimental conditions ranged from extremely rich to extremely lean. However, catalysts for these applications nowadays may contain material for the storage and release of NO$_x$, such as BaO (Fridell et al., 2000). The kinetic behaviour of the NO$_x$ storage can be added to the current model, or a derived form, in order enable the prediction of diesel and lean burn exhaust gas conversion, provided that particulate matter in diesel exhaust gases is mainly absent. This can be achieved by proper design of the diesel engine, which at the same time will result in a larger emission of NO$_x$.

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LIST OF PUBLICATIONS


List of publications


15. J.M.A. Harmsen, J.H.B.J. Hoebink, J.C. Schouten, Development of a kinetic model for the prediction of transient cold start behaviour of a commercial automotive exhaust gas catalyst, to be submitted to Applied Catalysis B: Environmental
CURRICULUM VITAE

Vanaf september 2001 is hij werkzaam bij Ford Motor Company te Aachen (Duitsland) bij de afdeling Diesel Powertrain Systems.
Verschillende mensen hebben een bijdrage geleverd aan het tot stand komen van dit proefschrift. Graag wil ik iedereen hiervoor van harte danken. Enkele mensen wil ik met name noemen:

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Stellingen

behorende bij het proefschrift

Kinetic modelling of the dynamic behaviour of an automotive three-way catalyst under cold-start conditions

van

Jan Harmsen

1. De efficiëntie van de NS als vervoerbedrijf zal sterk verbeteren, indien er niet alleen met treinen, maar ook permanent met bussen zou worden gereden.

2. Het gezegde, dat met vijf parameters een olifant beschreven kan worden, gaat alleen op voor stilstaande olifanten.

3. Het extrapoleren van reactiesnelheidsparameters over een temperatuurtraject van meer dan 100 K is niet gerechtvaardigd. (Hoofdstukken 5 en 6 van dit proefschrift)

4. De enige manier om de immense schoonheid van de orgelwerken van J.S. Bach volledig te doorgrijden, is door de werken zelf te spelen.

5. Een model, dat niet verbeterd kan worden, is geen model. (Hoofdstuk 6 van dit proefschrift)

6. De hoogte van de wegenbelasting moet niet alleen betrokken worden op het gewicht van de auto, maar ook op de hoeveelheid door de auto uitgestoten schadelijke componenten.

7. Het gebruik van propeen en propaan als model-koolwaterstoffen in een autouitlaatgas voor de beschrijving van de reactiekinetiek tijdens de koude start van een benzinemotor, is niet geïncludeerd.

8. Het verdwijnen van een bank en een postkantoor in combinatie met het verschijnen van een kapperszaak op de campus van een universiteit vormt geen afspiegeling van de behoeften van de universiteitmedewerkers.

9. Het ontbreken van enige stimulans voor het snel beoordelen van wetenschappelijke artikelen leidt tot grote en onnodige vertraging in de acceptatie en publicatie hiervan.

10. De verkeersveiligheid neemt toe, wanneer er een directe relatie wordt gelegd tussen de hoogte van de boete voor een verkeerstovertreding en de aard en omvang van het verkeersongeval, dat ten gevolge van de overtreding had kunnen ontstaan.

11. De kwaliteit van computersoftware neemt toe als een prestatiecontract, waarbij geld aan consumenten wordt teruggegeven bij het niet deugdelijk functioneren van een product, voor de software van toepassing zou zijn.