A reaction path analysis of the catalytic partial oxidation of methane by transient experiments

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A Reaction Path Analysis of the Catalytic Partial Oxidation of Methane by Transient Experiments

Erik Mallens
A Reaction Path Analysis of the Catalytic Partial Oxidation of Methane by Transient Experiments

Proefschrift

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de Rector Magnificus, prof.dr. M. Rem, voor een commissie aangewezen door het College van Dekanen in het openbaar te verdedigen op vrijdag 1 november 1996 om 16.00 uur

doors

Erik Petrus Johannes Mallens

geboren te Tilburg
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SUMMARY

The conversion of natural gas to transport fuels and petrochemicals has been intensively investigated due to an increasing excess of gas reserves over consumption. The high transportation costs over large distances are the driving force to develop processes to locally convert natural gas to more easily transportable chemicals.

The conversion of methane, the main component of natural gas, over different metal oxides and noble metals in the presence of dioxygen has been investigated in the framework of projects sponsored by the European Union. The target of the projects was to develop new processes for the conversion of methane to ethene, the so-called oxidative coupling of methane, and the conversion of methane to synthesis gas. These projects were carried out in collaboration with seven European universities and research institutes.

The research described in this thesis was focused on experimental work, carried out with a Temporal Analysis of Products (TAP) set-up. The microreactor of the TAP set-up can be considered as a batchwise operated fixed bed reactor with a typical residence time of 100 ms. Gaseous reactants are pulsed into the reactor and the responses are analysed by a quadrupole mass spectrometer. The amount of molecules in one pulse is typically far below the monolayer coverage, which means that the interactions of the reactants and reaction products with the catalyst surface are studied at a well-defined state of the catalyst. Pulses of pure methane, pure oxygen and mixtures of methane and oxygen are introduced into the reactor to study the reaction network. Moreover, pulses of oxygen followed by methane, ethane, ethene or carbon monoxide as well as pulses of methane and labelled oxygen were applied to study the role of adsorbed oxygen species and lattice oxygen in the reaction mechanism.
Equilibrium calculations were carried out to obtain insight into the thermodynamic stability of the possible species in the system oxygen/methane, oxygen platinum and oxygen/rhodium. At a methane to oxygen feed molar ratio of 0.5 the gas mixture at equilibrium solely consists of carbon dioxide and water at temperatures varying from 300 K to 1500 K. At ratios of 1, 2 and 3 the components methane, carbon dioxide, water and solid elementary carbon are present at low temperatures. At increasing temperature also carbon monoxide and hydrogen are present at equilibrium. The composition at high temperatures depends on the methane to oxygen feed molar ratio. At a ratio of 1 hydrogen, carbon monoxide, carbon dioxide and water are present, while at a ratio of 2 the gas mixture solely consists of hydrogen and carbon monoxide. Solid elementary carbon is also present at a ratio of 3 at high temperatures, besides hydrogen and carbon monoxide. Ethane and ethene were not present at equilibrium up to a methane to oxygen feed molar ratio of 3. Equilibrium calculations on the systems oxygen/platinum and oxygen/rhodium led to the conclusion that platinum oxide in the form of PtO₂ is stable from oxygen partial pressures of 6·10⁷ Pa on at a temperature of 1000 K. Rhodium oxide, in the form of Rh₂O₃, is already stable from oxygen partial pressures of 250 Pa on at the same temperature.

The oxidative coupling of methane has been studied in the presence of three catalysts based on magnesium oxide: MgO, Li/MgO and Sn/Li/MgO. The oxidative coupling of methane over Sn/Li/MgO in the presence of both methane and dioxygen at a temperature of 973 K proceeds as follows. Methyl radicals are produced at the surface and formation of ethane occurs in the gas phase via the coupling of two methyl radicals. Ethene is produced from ethane via a gas phase reaction in which dioxygen is involved. This reaction may involve surface produced ethyl radicals. Both ethane and ethene are oxidised to carbon monoxide at the surface. The oxidation of carbon monoxide to carbon dioxide proceeds via the surface. In parallel to the formation of ethane, methane is directly converted to carbon dioxide by a heterogeneous reaction.

Two types of adsorbed oxygen are present in the case of Sn/Li/MgO. The first type is strongly adsorbed oxygen, with a time scale for desorption amounting to three minutes at 973 K. This type of oxygen species is not active in the oxidative coupling reactions at all. The second type concerns weakly adsorbed oxygen species, which are completely desorbed after a time interval of four seconds at 973 K. This type of adsorbed oxygen species is involved in the direct conversion of methane to carbon dioxide.
Besides adsorbed oxygen also two types of surface lattice oxygen are present in the case of Li/MgO and Sn/Li/MgO. The first is active in the production of methyl radicals, while the second is active in the direct conversion of methane to carbon dioxide. Weakly adsorbed oxygen species and the second type of surface lattice oxygen are also active in the non-selective reaction paths of ethane and ethene as well as the consecutive oxidation of carbon monoxide.

The percentage of surface lattice oxygen which is active in the methane coupling reactions amounts to less than 0.1 % of a theoretical monolayer in the case of MgO at 1023 K. These values are 27 % for Li/MgO and 44 % for Sn/Li/MgO at the same temperature. The increase in the amount of active surface lattice oxygen as a result of the addition of lithium and moreover tin to magnesium oxide explains the increase in the activity of the catalysts in this order.

The partial oxidation of methane to synthesis gas has been investigated for platinum and rhodium sponge as catalyst. The interaction of pure dioxygen with reduced rhodium results in the complete oxidation to $\text{Rh}_2\text{O}_3$. Besides rhodium oxide also chemisorbed oxygen species are present, with a time scale for desorption amounting to two seconds. In the case of platinum only a partial oxidation occurs to an amount equivalent to 6 wt. % $\text{PtO}_2$. Besides platinum oxide also chemisorbed oxygen species and dissolved oxygen species are present. The dissolved oxygen species are completely desorbed after five minutes and the time scale for desorption of the chemisorbed oxygen species amounts to two seconds. The metal oxides are stable on an hour time scale. During the simultaneous interaction of methane and oxygen at a stoichiometric feed ratio for the production of synthesis gas only 0.4 wt. % $\text{Rh}_2\text{O}_3$ and 0.9 wt. % $\text{PtO}_2$ are present. The reaction occurs via a Mars-van Krevelen mechanism: methane reduces the metal oxide, which is reoxidised by dioxygen from the gas phase.

Methane dissociates to carbon and hydrogen adatoms on reduced surface sites. Synthesis gas is produced as primary product. Hydrogen is produced via the associative desorption of hydrogen adatoms and the reaction between carbon adatoms and oxygen in the form of platinum or rhodium oxide results in the formation of carbon monoxide. The consecutive oxidation of hydrogen and carbon monoxide occurs via both chemisorbed oxygen species and oxygen in the form of an oxide.

Rhodium is a more active catalyst for the conversion of methane and also shows a higher selectivity to synthesis gas, the selectivity to carbon monoxide being the most pronounced. The differences are explained by the higher activation energy of methane dissociation of platinum compared to rhodium.
A reaction path analysis of the catalytic partial oxidation of methane by transient experiments
SAMENVATTING

De omzetting van aardgas tot benzenes en gasolie of grondstoffen voor de petrochemische industrie wordt intensief onderzocht als gevolg van de grote voorraden van aardgas ten opzichte van het huidige verbruik. De hoge transportkosten van aardgas maken het noodzakelijk processen te ontwikkelen om het gas lokaal om te zetten tot makkelijker te transporteren chemicaliën.

De conversie van methaan, het belangrijkste bestanddeel van aardgas, over verschillende metaaloxide en edelmetalen in de aanwezigheid van zuurstof is onderzocht in het kader van projecten gesponsord door de Europese Unie. Het doel van deze projecten was het ontwikkelen van nieuwe processen voor de omzetting van methaan tot etheen, de zogenaamde oxidatieve methaankoppeling, en de omzetting van methaan tot synthesegas. Deze projecten zijn uitgevoerd in samenwerking met zeven Europese universiteiten en onderzoeksinstituten.

Het in dit proefschrift beschreven onderzoek heeft zich geconcentreerd op experimenteel werk uitgevoerd met een Temporal Analysis of Products (TAP) opstelling. De reactor van de TAP opstelling kan beschouwd worden als een ladingsgewijs bedreven vast-bed reactor met een typische verblijftijd van 100 ms. Gasvormige reactanten worden in de reactor gepulst en de uitgangssignalen worden geanalyseerd met behulp van een massaspectrometer. De hoeveelheid moleculen per puls is typisch veel lager dan een monolaagbedekking, resulterend in een goed gedefinieerde toestand van de katalysator voor de bestudering van de interactie van de reactanten en produkten met het oppervlak. Pulsen van puur methaan, puur zuurstof en mengsels van methaan en zuurstof zijn geïntroduceerd in de reactor voor bestudering van het reaktienetwerk. Daarnaast zijn pulseexperimenten van zuurstof gevolgd door methaan, etnaan, etheen of koolmonoxide alsmede mengsels van methaan en gelabeld zuurstof uitgevoerd om de rol van geadsorbeerd en roosterzuurstof in het mechanisme te onderzoeken.
A reaction path analysis of the catalytic partial oxidation of methane by transient experiments

Thermodynamische berekeningen zijn uitgevoerd om de relatieve stabiliteit te voorspellen van reactanten en reactieprodukten in de systemen zuurstof/methaan, zuurstof/platina en zuurstof/rhodium. Voor een initiële methaan tot zuurstof molaire verhouding van 0.5 bestaat het gasmengsel in de evenwichtstoestand bij temperaturen variërend van 300 K tot 1500 K slechts uit water en kooldioxide. Bij verhoudingen van 1, 2 en 3 zijn de componenten methaan, water, kooldioxide en vast elementair koolstof aanwezig bij lage temperaturen. Bij toenemende temperatuur zijn tevens koolmonoxide en waterstof aanwezig. De samenstelling bij thermodynamisch evenwicht hangt voor hogere temperaturen af van de initiële methaan tot zuurstof molaire verhouding. Bij een verhouding van 1 bestaat het gasmengsel uit waterstof, koolmonoxide, water en kooldioxide, terwijl bij een verhouding van 2 alleen koolmonoxide en waterstof voorkomen. Behalve koolmonoxide en waterstof is tevens vast elementair koolstof aanwezig bij een initiële verhouding van 3 en hoge temperaturen. Ethaan en etheen zijn niet aanwezig bij evenwicht tot op een initiële methaan tot zuurstof molaire verhouding van 3. Uit de berekeningen voor de systemen zuurstof/platina en zuurstof/rhodium is geconcludeerd dat een platinaoxide fase in de vorm van PtO₂ stabiel is voor zuurstofpartiaalspanningen van $6 \times 10^7$ Pa en hoger, bij een temperatuur van 1000 K. Rhodiumoxide, in de vorm van Rh₂O₃, is al stabiel bij zuurstofpartiaalspanningen van 250 Pa en hoger bij dezelfde temperatuur.

De oxidatieve methaankoppeling is bestudeerd in aanwezigheid van drie op magnesiunoxide gebaseerde katalysatoren: MgO, Li/MgO en Sn/Li/MgO. De oxidatieve methaankoppeling over Sn/Li/MgO in aanwezigheid van methaan en zuurstof bij een temperatuur van 973 K verloopt als volgt. Methylradicalen worden geproduceerd aan het oppervlak en de vorming van ethaan vindt plaats in de gasfase door de koppeling van twee methylradicalen. Ethaan wordt gevormd uit etaan door middel van een reaktie in de gasfase met behulp van zuurstof, welke waarschijnlijk verloopt via het oppervlak geproduceerde ethylradicalen. Ethaan en etheen worden aan het oppervlak van de katalysator geoxideerd tot koolmonoxide. De oxidatie van koolmonoxide tot kooldioxide vindt plaats aan het oppervlak. Parallel aan de vorming van ethaan wordt methaan direct omgezet tot kooldioxide via een heterogene reaktie.

Twee typen geadsorbeerde zuurstof zijn aanwezig in het geval van Sn/Li/MgO. Het eerste type is sterk geadsorbeerde zuurstof, waarvoor de tijdschaal van desorptie drie minuten bedraagt bij 973 K. Dit type zuurstof is niet aktief in de methaankoppeling reakties. Het tweede type is zwak geadsorbeerde zuurstof met een tijdschaal van desorptie van vier seconden bij 973 K. Dit type zuurstofspecies speelt een rol in de direkte omzetting van methaan tot kooldioxide.
Naast geadsorbeerd zuurstof bestaan in het geval van Li/MgO en Sn/Li/MgO nog twee verschillende typen oppervlak roosterzuurstofatomen. De eerste is aktief in de produktie van methylradicalen en de tweede is aktief in de direkte omzetting van methaan tot kooldioxide. Zwak geadsorbeerd zuurstof en het tweede type roosterzuurstof zijn ook aktief in de niet-selectieve reaktiepaden van etaan en etheen en in de consecutieve oxidatie van koolmonoxide.

Het percentage oppervlak roosterzuurstofatomen dat aktief is in de omzetting over MgO bedraagt minder dan 0.1 % van een theoretische monolaag bij 1023 K. Deze waarde bedraagt 27 % voor Li/MgO en 44 % voor Sn/Li/MgO bij dezelfde temperatuur. De toename in de hoeveelheid aktieve roosterzuurstofatomen als gevolg van de toevoeging van lithium en bovenal tin aan magnesiumoxide verklaart de toename in de activiteit van de katalysatoren in deze volgorde.

De partiële oxidatie van methaan tot syntheseoas is onderzocht voor platina en rhodium spons als katalysator. De interactie van puur zuurstof met rhodium resulteert in complete oxidatie tot Rh$_2$O$_3$. Naast rhodiumoxide is ook gechemisorbeerd zuurstof aanwezig, met een tijdschaal voor desorptie van twee seconden. In het geval van platina vindt slechts partiële oxidatie plaats tot een hoeveelheid equivalent aan 6 wt. % PtO$_2$. Echter, behalve platinaoxide zijn ook gechemisorbeerd zuurstof en opgeloste zuurstofspecies aanwezig. Het opgeloste zuurstof is volledig gedesorbeerd na vijf minuten en de tijdschaal voor desorptie van het gechemisorbeerd zuurstof bedraagt twee seconden. De metaaloxide zijn stabiel op een tijdschaal van uren. Tijdens de simultane interactie van methaan en zuurstof bij een stoichiometrische voedingsverhouding voor de produktie van syntheseoas is slechts 0,4 gew. % Rh$_2$O$_3$ en 0,9 gew. % PtO$_2$ aanwezig. De reaktie verloopt via een Mars-van Krevelen mechanisme: methaan reduceert het oxide dat gereoxideerd wordt door zuurstof uit de gasfase.

Methaan dissociëert op gereduceerde centra tot geadsorbeerd koolstof en waterstof. Synthesizeoas wordt geproduceerd als primair produkt. Waterstof wordt gevormd via de associatieve desorptie van waterstofadatomen en de reaktie tussen koolstofadatomen en zuurstof en koolstof in de vorm van rhodium- of platinaoxide resulteert in de vorming van koolmonoxide. De consecutieve oxidatie van waterstof en koolmonoxide vindt plaats via zowel gechemisorbeerd zuurstof als zuurstof aanwezig als oxide.

Rhodium is een aktiever katalysator voor de omzetting van methaan dan platina en vertoont een hogere selectiviteit naar syntheseoas, met name naar koolmonoxide. Het verschil wordt verklaard door de hogere aktiveringsenergie voor methaanaktivering voor platina in vergelijking met rhodium.
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<th>Symbol</th>
<th>Description</th>
<th>Units</th>
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<td>external catalyst surface area per unit catalyst volume</td>
<td>$\text{m}_c^2 \text{m}_c^{-3}$</td>
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<td>$A_s$</td>
<td>cross section area of the reactor</td>
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A reaction path analysis of the catalytic partial oxidation of methane by transient experiments

\( x \) \hspace{1cm} \text{axial coordinate in reactor} \hspace{1cm} \text{m}

\( X \) \hspace{1cm} \text{conversion} \hspace{1cm} \text{mol mol}^{-1}

\( Y \) \hspace{1cm} \text{yield} \hspace{1cm} \text{mol mol}^{-1}

\textbf{Greek symbols}

\( \varepsilon_b \) \hspace{1cm} \text{bed porosity} \hspace{1cm} m_g^3 m_r^{-3}

\( \tau_b \) \hspace{1cm} \text{bed tortuosity} \hspace{1cm} m_g^2 m_r^{-2}

\( \theta \) \hspace{1cm} \text{fractional coverage on the catalyst surface}

\( \epsilon \) \hspace{1cm} \text{mass balance} \hspace{1cm} \text{mol mol}^{-1}

\( \sigma \) \hspace{1cm} \text{stoichiometric number}

\( \tau \) \hspace{1cm} \text{time scale} \hspace{1cm} s

\textbf{Subscripts}

\( A \) \hspace{1cm} \text{with respect to A}

\( \text{ads} \) \hspace{1cm} \text{adsorption}

\( b \) \hspace{1cm} \text{bed; interstitial voids}

\( \text{des} \) \hspace{1cm} \text{desorption}

\( \text{diff} \) \hspace{1cm} \text{Knudsen diffusion}

\( * \) \hspace{1cm} \text{vacant sites}
1

GENERAL INTRODUCTION

Background

The conversion of natural gas has been intensively studied over the past decade. The interest in using natural gas as a source of petrochemicals and transport fuels was caused by an increasing excess of gas reserves over consumption and a high price of oil, peaking at about US$ 40 per barrel in 1981. Economic forecasts in the beginning of the eighties were based on oil prices at this level, or even higher up to US$ 100 per barrel. At the present time, the price of oil has dropped to US$ 18 per barrel and only a modest increase for the rest of this decade is expected, which makes it more difficult to develop economically attractive processes for the conversion of natural gas. World proven gas reserves are estimated at 135 $10^{12}$ Nm$^3$ and at current production levels, reserves are adequate for a further 66 years (Shell International Petroleum Company Limited, 1995). Figure 1.1 shows the world proven natural gas reserves in 1994. The former Soviet Union has the largest reserves amounting to 40 % of the total, followed by Iran with 15 %. Most natural gas is consumed locally since large distance transportation involves high costs to increase the energy density, which is low as compared to that of petroleum liquids. By contrast, the cost of transportation of liquids, such as oil or methanol, does not add more than 10 % to the cost of product delivered at the point of use (Parkyns et al. (1993). This explains the driving force for siting methane conversion plants where the natural gas is cheapest.

Methane is the main component of natural gas and the most stable of all hydrocarbons. The conversion of methane to higher hydrocarbons requires dehydrogenation and subsequent coupling of the C$_1$ building blocks.
A reaction path analysis of the catalytic partial oxidation of methane by transient experiments

Figure 1.1: World proven natural gas reserves in 1994 (Shell International Petroleum Company Limited, 1995).

Two routes can be distinguished: a direct or an indirect dehydrogenation route, the latter mainly via CO and H₂ as intermediates. Examples of direct dehydrogenation processes are the pyrolysis of methane and the oxidative dehydrogenation via oxygen, chlorine or sulfur species (Lange, 1994). However, these processes require oil prices in the range of US$ 30 - 40 per barrel to become economically attractive at the presently obtainable yields (Lange, 1994). The main problem of the direct dehydrogenation route is that the desired products are much more reactive than methane and the challenge is to avoid their further conversion to CO₂ or coke. The oxidative coupling of methane is the most intensively studied direct conversion process during the past decade. The process aims at the production of ethene, typically proceeds at temperatures between 900 and 1200 K, at pressures between 100 and 1000 kPa and under methane rich conditions in the presence of a heterogeneous catalyst. An important reason for the interest in the oxidative coupling of methane is that ethene is a product which would allow a high added value to that of natural gas (Parkyns et al., 1993). At this moment the maximum attainable yield is in the order of 20 - 25 % of methane in the feed (Parkyns et al., 1993).

In the indirect dehydrogenation route, synthesis gas, a mixture of CO and H₂, is often used as intermediate. Presently, the most important industrial route to synthesis gas is the endothermal steam-reforming of methane. A high temperature is applied during this process to thermodynamically favour the conditions for
synthesis gas formation, see section 3.2.2. The hydrogen to carbon monoxide molar ratio in the product mixture amounts to three and is often modified in a second reactor by means of the reverse water-gas shift reaction to the more favourable value of 2 for most downstream processes. A promising alternative for the production of synthesis gas is the direct partial oxidation of methane to synthesis gas over supported transition metals, due to the more favourable $H_2$ to CO ratio in the product gas as well as the exothermicity of the reaction (Hickman and Schmidt, 1993). The contact times are approximately $10^{-3}$ s, compared to 1 s for the steam reforming reaction, which strongly reduces the reactor volume for a given production rate.

Synthesis gas can be directly converted to higher hydrocarbons via the Fischer-Tropsch reaction, by the polymerization of CH$_x$ fragments. A disadvantage of the originally developed Fischer-Tropsch process, which focused on direct middle distillate formation, is the formation of a wide range of hydrocarbons. The recently developed Shell Middle Distillates Synthesis process involves an advanced Fischer-Tropsch process with a high polymerization selectivity, leading to long-chain wax growth. The heavy product fraction is subsequently converted to the desired fuel fraction by means of mild cracking. Synthesis gas conversion to methanol is a second important application of the indirect dehydrogenation of natural gas. Besides as a feedstock for the chemical industry, methanol can also be converted to higher hydrocarbons via the methanol-to-olefins or methanol-to-gasoline processes.

**Role of transient kinetic research**

Kinetic models describe in a mathematical way the dependence of the reaction rates on the process conditions and form the basis for the design and optimisation of chemical reactors. Most kinetic research is being carried out at steady-state conditions, when the time scale of change in the process conditions is much larger when compared to the times scale of the elementary reaction steps. In the steady-state approximation the accumulation of intermediates is neglected i.e. the rates of all elementary reaction steps in series, making up the global reaction, are balanced. Resulting kinetic rate equations often correspond to more than one reaction mechanism and the kinetic parameters estimated by regression of the kinetic model to the data usually are combinations of reaction rate coefficients of elementary reaction steps.

Transient kinetic research is an alternative approach for studying reaction kinetics, in which perturbations are introduced by changing one or more of the state variables, such as feed concentration, molar flow rate, pressure or
temperature. Perturbations could be implemented as pulses, step-wise changes or periodic cycling. Transient kinetic experiments have the potential to provide information on the kinetics of elementary reaction steps, because the steady-state approximation cannot be applied anymore on the reactive intermediates. The perturbation should be imposed on a time scale small compared to the time scale of at least the sequence of elementary reaction steps, i.e. the time interval that allows a sequence of elementary steps to reach the steady-state after an instantaneous perturbation.

Until recently, transient kinetic experiments in heterogeneous catalysis could be performed with a time resolution of about one second. The latter was limited by both the introduction of the perturbation and the analysis of the response signal. Gleaves and coworkers developed the Temporal Analysis of Products (TAP) set-up (Gleaves et al., 1988), which operates at a millisecond time scale, two orders of magnitude better than the conventional transient techniques. The improvement was achieved by paying attention to both limiting factors mentioned above. The TAP set-up and the type of experiments than can be performed applying this set-up are described in detail in Chapter 2.

Scope of this thesis

This thesis deals with the oxidative coupling of methane to ethane/ethene and with the catalytic partial oxidation of methane to synthesis gas. On the oxidative coupling of methane kinetic research is reported in the presence of a tin promoted lithium on magnesium oxide catalyst. The lithium on magnesium oxide catalyst was first described by Ito et al. (1985). The highest yield to ethane and ethene obtained on this catalyst with undiluted feed gases amounts to 19 % of the methane in the feed (Ekström et al., 1990). However, the life time of this catalyst is very poor and therefore Korf et al. (1989) investigated the promotion of lithium on magnesium oxide with a reducible metal oxide. Tin was found to be one of the best additives among many elements tested, because it increases the life time of the catalyst with a simultaneous increase in activity.

The elementary reactions in the catalytic oxidative coupling of methane are not completely understood yet, especially those leading to side products. In this thesis the reaction network of the oxidative coupling of methane over tin promoted lithium on magnesium oxide has been investigated in detail by means of transient kinetic experiments. The proposed mechanism distinguishes between catalytic reaction steps and homogeneous reactions in the gas phase. Emphasis has been put on the role of both surface lattice oxygen and adsorbed oxygen in the reaction mechanism, since this leads to fundamental insight into the role of the catalyst in
the non-selective reaction paths. Also, the roles of lithium and tin in the tin promoted lithium on magnesium oxide catalyst were clarified.

The catalytic partial oxidation of methane to synthesis gas has been studied in the presence of both platinum and rhodium sponge catalyst. On platinum and on rhodium selectivities to synthesis gas of 90 % or more were reported (Hickman and Schmidt, 1993).

The reaction mechanism of the catalytic partial oxidation of methane was investigated in detail and the reaction paths were analysed in terms of primary and secondary product formation, since this point is still in debate. The emphasis was put on obtaining information for a catalyst which was at steady-state in an environment as typical as possible for the partial oxidation: i.e. a temperature of 1100 K and a gas phase consisting of methane and oxygen in a feed molar ratio of 2. The oxygen pathways were thoroughly studied and the role of both adsorbed and incorporated oxygen in the reaction was explained, especially for the non-selective reaction paths. The differences between platinum and rhodium as catalysts for the partial oxidation of methane were addressed as well.

References


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2

EXPERIMENTAL SET-UP AND PROCEDURES

2.1 Introduction

All experiments presented in this thesis are carried out with a Temporal Analysis of Products (TAP) set-up. The TAP set-up, developed by Gleaves and co-workers (Gleaves et al., 1988), is a catalyst characterisation and evaluation set-up, in which a microreactor is encased within a high vacuum chamber. The microreactor can be considered as a batchwise operated fixed bed reactor with a typical residence time of 100 ms. Gaseous reactants are either continuously fed or pulsed into the reactor and mass spectrometry is used to follow the outlet responses. Primarily the TAP set-up is to be used as a pulsed reactor. It allows transient experiments to be carried out on a millisecond time scale, which is two orders of magnitude faster than with conventional transient experimental set-ups for studying heterogeneously catalysed reactions. It allows to study catalytic sequences in detail, even at a high conversion. A limited amount of molecules, typically far below the monolayer coverage, is admitted to the catalyst surface, leading to information about the interaction of reactants and products with the catalyst at a well-defined state of the latter.

In section 2.2 the TAP apparatus is described. Section 2.3 deals with the types of experiments, that can be performed with the TAP set-up. The determination of the absolute calibration factors of the components involved is described in this section as well. The purity of the gases used in the experimental work is presented in section 2.4. Section 2.5 deals with the characterisation and pretreatment of the catalysts used during the experimental work.
2.2 The TAP set-up

The TAP set-up was described in detail by Gleaves et al. (1988), Statman (1991), Svoboda (1993) and Huinink (1995). Only the aspects relevant to the present work will be considered here. The hardware of the Temporal Analysis of Products set-up includes seven main components:

1. a vacuum system providing high vacuum conditions in three chambers;
2. a gas manifold assembly to which two continuous flow valves and two pulse valves are connected;
3. a microreactor;
4. a high pressure assembly, allowing reactor pressures up to \(2 \times 10^5\) Pa;
5. a quadrupole mass spectrometer (QMS) detector;
6. a gas preparation section;
7. a computerized data acquisition and control system.

Figure 2.1 shows a schematic view of the vacuum system of the TAP set-up. All relevant details will be discussed below.

![Figure 2.1: Schematic view of the vacuum system of the TAP set-up.](image)
Experimental set-up and procedures

Vacuum system

The vacuum system of the TAP set-up consists of three vacuum chambers, see Figure 2.1. Inside the reactor chamber the manifold assembly with continuous and pulse valves, the microreactor and the high pressure assembly are positioned. Vacuum is realised by a water-cooled 10" Varian VHS10 oil diffusion pump and a Varian SD700 mechanical pump. The pressure inside the reactor chamber typically amounts to $10^{-5}$ Pa as measured with a Varian #580 ion gauge. The differential chamber is located between the reactor chamber and the analytical chamber. Vacuum in the differential chamber is provided by a water-cooled 6" Varian VHS6 oil diffusion pump with a liquid nitrogen trap and a Varian SD700 mechanical pump. The trap improves the chamber's vacuum by preventing that oil of the diffusion pump reaches the detector chamber. Vacuum in the analytical chamber, which contains the ionisation head of the UTI 100C quadrupole mass spectrometer, is provided by a Balzers TPU450H turbomolecular pump, in series with a Baltzers MD4TC diaphragm pump. The pressures in the differential and analytical chambers are measured with a Balzers IKR020 cold cathode gauge head and are typically $10^{-6}$ and $10^{-7}$ Pa. The differential chamber prevents molecules to reach the mass spectrometer at a later time, when they do not directly pass through to the quadrupole mass spectrometer but in some way are deflected. The deflected molecules are pumped away. In this way peak broadening after leaving the reactor is minimised. A shutter valve is present to fully isolate the reactor chamber from the differential chamber, which permits the microreactor to be removed and recharged without disturbing the vacuum conditions in the differential and analytical chamber.

Manifold assembly with continuous and pulse valves

The stainless steel manifold assembly, see Figure 2.2, has six entries. Two entries are occupied by continuous flow valves, two by pulse valves, one by the microreactor and one entry is not used. Two cartridge heaters are inserted in the manifold assembly and during experiments the temperature of the assembly and the valves is controlled by an Eurotherm temperature controller at a setpoint of 343 K. Variations in temperature would influence the performance of the valves. The dead volume of the intersection of all entries is less than 1 μl.

The continuous flow valves are controlled pneumatically in order to eliminate their heating due to electrical resistance. The pulse valve interior is divided into two separate chambers by a small stainless steel bellow, as shown in Figure 2.2. A pressure difference of 10 kPa is maintained between the chamber filled with reactant gas, and the back pressure chamber filled with nitrogen gas, to ensure
that the valve exit is sealed when not using the pulse valve. The pulse valve is opened via an electrical current through the opening coil and simultaneously the current through the closing coil is stopped. The current for both coils is supplied by a Newport Corporation BV100 beam valve driver.

The ferromagnetic field activates a magnetic disc attached to the valve stem, which lifts the stem from the valve exit. A few microseconds later, the beam valve driver stops the current through the opening coil and the valve is maximally opened at this moment. Again after a few microseconds the closing coil is activated and via the reversed magnetic field the valve is closed. The pulse valves can generate up to 40 pulses per second. The amount of molecules introduced per pulse, the pulse intensity, is determined by the reactant gas pressure in the front chamber and the time between opening and closing the valve. The pulse intensity depends on the stem length adjustment as well. The open-to-close time can be adjusted with the beam valve driver. In this way, the pulse valve can introduce $10^{13}$ up to $10^{19}$ molecules per pulse with a minimal pulse width on half height of 200 $\mu$s.

*Figure 2.2:* Schematic representation showing TAP microreactor, furnace, manifold assembly and one pulse valve.
Experimental set-up and procedures

Microreactor

The microreactor, shown in Figure 2.2, is a hollow cylinder of inconel steel with an overall length of 47.2 mm and an inner diameter of 5.6 mm. The inlet of the microreactor is sealed by a Viton or Kalrez O-ring and the outlet contains a sealing flange to connect optionally the high pressure assembly with the reactor.

The radiant furnace, see Figure 2.2, provides heating of the reactor, which can be operated from ambient to 1273 K. The radiant furnace covers only the major middle part of the microreactor. The reactor temperature is controlled via a thermocouple in the reactor wall. Two thermocouples were inserted into the catalyst bed for inside temperature measurements. The O-ring at the inlet is cooled. The outlet O-ring sealing is also cooled to allow the use of the high pressure assembly. As a result a temperature profile over the microreactor is established, as shown in Figure 2.3 for different reactor wall temperatures.

![Temperature Profile](image)

**Figure 2.3:** Temperature profile in the packed bed of the microreactor at a temperature of the reactor wall of: 298 (+), 373 (△), 473 (○), 573 (□), 673 (■), 773 (●), 873 (▲) and 973 K (◇). (Huinink, 1995)

The middle part of the reactor, in the range of 10-23 mm from the inlet, is isothermal within 5 K at wall temperatures from ambient to 1000 K, see Figure 2.3. The catalyst bed was always positioned in the isothermal part of the microreactor and enclosed with an inert material on both sides. Gauze screens on
both sides of the reactor packing keep the bed in position.

**High pressure assembly**

The high pressure assembly allows experiments to be carried out at pressures up to $2 \times 10^5$ Pa. The assembly seals the outlet of the microreactor and gases at the reactor outlet are led through a vent valve. It is possible to link the vent valve to a gaschromatograph, in order to analyze the outlet gases. The high pressure assembly also contains a pinhole leak valve, which allows a small fraction of the outlet gases to reach the quadrupole mass spectrometer for time-resolved analysis. The high pressure assembly was not used for the work presented in this thesis.

**Quadrupole mass spectrometer**

Analysis of the responses towards a continuous flow or pulses of reactants admitted at the reactor inlet, is carried out with a UTI 100C quadrupole mass spectrometer, located in the analytical chamber with its axis mounted perpendicular to the axis of the microreactor. The analysis can be in a time-resolved or mass scan mode, see section 2.3.1. The mass spectrometer measures the molar flow rate of a component in amperes. Absolute calibration is possible and is described in section 2.3.2. The mass spectrometer produces analog signals, which can be directly observed with an oscilloscope or digitized by the data acquisition system, and operates between Atomic Mass Unit (AMU) values of 1 to 300. The mass resolution, expressed as full width at half height, is 0.5 AMU.

**Gas preparation section**

Reactant gases are fed to the continuous flow valves and the pulse valves via the gas preparation section. The preparation section allows to prepare reactant mixtures at well defined reactant ratios, and to feed them at a constant pressure to the valves. Two small vessels of about 150 cm$^3$ are present to store the reactant gases. Gas mixtures in the storage vessels are prepared by measuring the pressure increase with two Setra Model 280E/C280E pressure indicators with an accuracy of 7 mbar. In this way, many experiments can be carried out without the need to refill the vessels. When preparing gas mixtures, the vessels insure the gases to be perfectly mixed. In isotopic experiments the vessels are not used because of the high amount of gas which is needed to fill a vessel and in this case only the tubing of the gas preparation section between the vessels and the valves is used. Mechanical vacuum pumps are present to allow operation below atmospheric pressure and evacuation of the tubing and vessels prior to preparing
a different gas mixture.

Control and data acquisition

A HP 360 workstation is attached to the following parts of the TAP set-up: the HP 3865A data acquisition/control unit, the UTI 100 SpectraLink, the two Newport BV100 beam valve drivers and the Eurotherm 818P temperature controller.

With the TAP software, installed on the workstation, data from the quadrupole mass spectrometer can be stored, analyzed and plotted. The data acquisition unit can gather up to 10,000 data points per 0.1 s. The workstation regulates the pulse valves via the beam valve drivers. The different types of experiments, which are described in detail in section 2.3.1, are carried out and controlled via the software. The temperature of the microreactor can be set and the quadrupole mass spectrometer can be adjusted to monitor a specific AMU value. A detailed description of the possibilities is given by the Autoclave Engineers Group (1991).

2.3 Experimental procedures

In section 2.3.1 all types of experiments, that can be performed with the TAP set-up, are discussed. The determination the absolute calibration factors is described in section 2.3.2. In section 2.3.3 the procedure for smoothing of the responses is described. The signal analysis is discussed in section 2.3.4.

2.3.1 Types of experiments

The design of the manifold, with two pulse valves and two continuous valves, and the high pressure assembly combined with the HP data acquisition and control system, allows several experimental formats. The mass spectrometer can be operated in two basic modes. In the scan mode, the mass spectrometer is set to scan a specified mass range. In the pulse mode, the mass spectrometer is fixed at a specific AMU value and the intensity of the specified mass is measured during a specified time.

Scan experiment

In a scan experiment a steady flow, amounting to $10^{-6} \text{ mol s}^{-1}$, of the reactant gas(es) is fed to the microreactor via the continuous flow valve. The
average pressure in the microreactor amounts to $10^4$ Pa during the steady flow. The quadrupole mass spectrometer is set to scan a user-specified mass spectrum. In a scan experiment a plot of the mass intensity in ampere versus the AMU value is measured and a typical result is shown in Figure 2.4.

![Figure 2.4: Typical result of a scan experiment](image1)

**Pulse experiment**

Transient experiments were performed in three different ways. The first type is referred to as a pulse experiment. During a pulse experiment the response to a single pulse is monitored at a fixed AMU value. Pulses are repeated regularly and the responses are averaged to improve the signal-to-noise ratio. A typical result of a pulse experiment is shown in Figure 2.5.

![Figure 2.5: Typical result of a pulse experiment](image2)
The repetition time is chosen sufficiently large to avoid accumulation of adsorbed species at the catalyst surface. This sequence is repeated for each AMU value to be measured.

**Alternating pulse experiment**

The second type of transient experiment is referred to as an alternating pulse experiment, also called pump-probe experiment (Gleaves et al., 1988). Two single pulses are subsequently introduced at a user-specified time interval and the response is measured at a fixed AMU value. By varying the time interval between the two single pulses information on life time and reactivity of adsorbed species is obtained. These species are created during the first pulse and probed with a suitable reactant during the second pulse. As in the case of a pulse experiment, pulses are repeated at a chosen repetition time and the responses are averaged to improve the signal-to-noise ratio.

**Multi pulse experiment**

The third type of transient experiment concerns a multi pulse experiment. A series of pulses is introduced and the responses of all pulses are monitored separately, i.e. without signal averaging, at a fixed AMU value, see Figure 2.6. The time interval between two subsequent pulses is variable and must be larger than the average residence time in the reactor to avoid accumulation of components in the void space of the catalyst bed, resulting in base-line drift. A multipulse experiment can be used to study the interaction of a component with the surface at different degrees of surface coverage.

![Figure 2.6: Typical result of a multi pulse experiment](image)
2.3.2 Calibration factor determination

For a quantitative interpretation of the pulse responses, the absolute calibration factor of each component has to be determined. The measured response is an electric current corresponding to a molar flow rate at the reactor outlet. The integration of the responses provides the peak surface areas, which are a measure for the amount of molecules leaving the reactor per pulse. An absolute calibration factor relates the peak surface area to the amount of molecules. Determination of the absolute calibration factor is carried out for each reactant or reaction product, except water, by allowing a steady flow from the gas preparation section through the microreactor, packed with inert material only, during a specific time, while monitoring the constant QMS-signal and the pressure decrease in the gas storage vessel. Applying the ideal gas law, the absolute calibration factor can be calculated with the following expression:

\[
C_i = \frac{\Delta p_i V}{R T \Delta t I_{QMS}}
\]  

(2.1)

where \( \Delta p_i \) is the pressure decrease of component i in the vessel (Pa), \( V \) is the vessel volume (m\(^3\)), \( \Delta t \) is the release time (s), \( C_i \) is the absolute calibration factor of component i (mol C\(^{-1}\)) and \( I_{QMS} \) the electric current measured by the quadrupole mass spectrometer (C s\(^{-1}\)). The absolute calibration factor of water was deduced from the value of carbon dioxide, see section 2.5.2.1.

The absolute calibration factor of a component is dependent on the pressure in the analytical chamber. The higher the pressure in the analytical chamber, the lower the calibration factor, due to the higher electric current measured by the mass spectrometer. Each week the absolute calibration factors of all components were determined at a certain pressure. The ratio of the absolute calibration factor of a component to the value of argon was shown to be independent of the pressure in the analytical chamber and is identical for all components involved. Therefore it is sufficient to determine every day the absolute calibration factor of the reference component argon, only. The absolute calibration factors of the other components can then be calculated from the previously determined ratios.

The absolute calibration factor is also dependent on the reactor temperature. Due to a higher kinetic energy of the molecules arriving in the ionisation chamber, ionisation becomes more pronounced at higher reactor temperature. The measured signal at the AMU value of the unfragmented component becomes smaller. However, the ratio of absolute calibration factor to the value of argon is independent of temperature and identical for all components. The calibration factor of a component at reaction temperature is calculated from the value of argon at that temperature and the ratio of the absolute calibration factor to the value of
argon at 373 K. The absolute calibration factor depends also on the multiplier voltage of the mass spectrometer.

**Table 2.1:** Typical absolute calibration factors of reactants and reaction products at 373 K and 973 K. Numbers in italics were calculated from the measured values, shown in normal script. Electron Energy: 70 eV, Multiplier Voltage: 1.5 kV and pressure in the analytical chamber: \(1.2 \times 10^{-7}\) mbar.

<table>
<thead>
<tr>
<th>component</th>
<th>373 K mol C(^{-1})</th>
<th>973 K mol C(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>0.10</td>
<td>0.14</td>
</tr>
<tr>
<td>O(_2)</td>
<td>0.22</td>
<td>0.31</td>
</tr>
<tr>
<td>C(_2)H(_6)</td>
<td>0.33</td>
<td>0.46</td>
</tr>
<tr>
<td>C(_2)H(_4)</td>
<td>0.18</td>
<td>0.25</td>
</tr>
<tr>
<td>CO</td>
<td>0.13</td>
<td>0.18</td>
</tr>
<tr>
<td>CO(_2)</td>
<td>0.14</td>
<td>0.20</td>
</tr>
<tr>
<td>H(_2)</td>
<td>0.25</td>
<td>0.35</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>0.27</td>
<td>0.38</td>
</tr>
</tbody>
</table>

The absolute calibration factors of Ar, CH\(_4\), O\(_2\), C\(_2\)H\(_6\), C\(_2\)H\(_4\), CO, CO\(_2\), H\(_2\) and H\(_2\)O at 373 K are listed in Table 2.1. The absolute calibration factor of Ar was also determined at 973 K. The calibration factors of the other components at 973 K were calculated from the ratios of the calibration factors at 373 K and printed in italics in Table 2.1.

2.3.3 Curve smoothing

Besides signal averaging smoothing of the response is also applied to improve the signal-to-noise ratio, in case the amount of molecules to be detected is in the range of \(10^{13} - 10^{14}\). The latter is necessary for an accurate determination of the peak surface area. A smoothing routine from Rothaemel (1993) was used, applying the Fast Fourier Transform (FFT) method for optimal filtering of the signal, as described in detail by Press *et al.* (1992). The routine allows to adjust the window size to minimize changes in the shape of the response curve due to smoothing. The original and smoothed response were always compared. In Figure 2.7 a part of a measured and a smoothed response to a single pulse of argon is shown. The result of the smoothing is quite satisfactory.
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Figure 2.7: Part of a measured and smoothed response of a single pulse experiment with argon.

2.3.4 Signal analysis

2.3.4.1 Time resolution

The TAP set-up is designed to operate at a millisecond time scale. This is accomplished by injecting an extremely narrow gas pulse into the microreactor. The minimal inlet pulse width at half height is about 200 μs and is negligible compared to the time scale of gas transport through a packed bed of about 100 ms. The sensitivity of the mass spectrometer is limited by the real time analysis requirements of a TAP experiment. At increasing sensitivity of the electron multiplier, the time constant of the mass spectrometer also increases. For most experiments it is necessary to have a time constant less than 0.2 ms, which limits the sensitivity of the UTI multiplier to \(10^{-10}\) A (UTI Instruments Co., 1990). The differential chamber prevents molecules, that do not directly pass through to the quadrupole mass spectrometer but in some way are deflected, to reach the mass spectrometer at a later time. Except for light gases such as hydrogen and helium, less than 0.1 % of the detected pulse results from scattered molecules (Gleaves et al., 1988).
2.3.4.2 Reaction network analysis

The TAP set-up is a very powerful tool for studying the network of complex reactions by comparison of the responses of all reaction products. The shape of a response is determined by the various processes occurring in the microreactor: gas transport through the packed bed as well as adsorption, desorption and reaction at the catalyst surface. Each response has a unique rise time, peak maximum and decay curve.

A plot of the responses as a function of time contains in principle information on the reaction network. A secondary product has a response with a larger rise time than a primary product and its peak maximum is observed later. Adsorption and desorption processes result in a shift of the peak maximum towards a larger time value. The position of the peak maximum is also determined by the molecular weight of the component via the Knudsen diffusion coefficient. The peak maximum of a reactant response shifts to the left and the peak height is reduced as a result of the conversion of the reactants.

2.4 Gases used in the experiments

In Table 2.2 the gases used in the experimental work are listed, together with their purity and supplier. In order to determine or verify fragmentation patterns of the gases, scan experiments were performed by admitting a steady flow of a pure component through the microreactor, packed with inert $\alpha$-Al$_2$O$_3$ only, except for $^{18}$O$_2$. The fragmentation patterns are dependent of the temperature, as explained in section 2.3.2., and should therefore be recorded at reaction temperature.

<table>
<thead>
<tr>
<th>gas</th>
<th>purity</th>
<th>supplier</th>
<th>gas</th>
<th>purity</th>
<th>supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>99.9999</td>
<td>Hoekloos</td>
<td>CO$_2$</td>
<td>99.999</td>
<td>Air Products</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>99.995</td>
<td>Air Products</td>
<td>H$_2$</td>
<td>99.999</td>
<td>Air Products</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>99.995</td>
<td>Air Products</td>
<td>O$_2$</td>
<td>99.9999</td>
<td>Air Products</td>
</tr>
<tr>
<td>C$_2$H$_4$</td>
<td>99.995</td>
<td>Air Products</td>
<td>$^{18}$O$_2$</td>
<td>99.95</td>
<td>Union Carbide</td>
</tr>
<tr>
<td>CO</td>
<td>99.9997</td>
<td>Hoekloos</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2.2: Gases used in the experimental work.
2.5 Catalysts

2.5.1 MgO based catalysts

Three different catalysts were used in the various experiments on the oxidative coupling of methane: MgO, Li/MgO and Sn/Li/MgO. The MgO catalyst was prepared by pelletising MgO powder (Merck) followed by crushing and sieving to a size range 0.15 - 0.21 mm. The Li/MgO catalyst was prepared by precipitation of LiOH on Mg(OH)₂, as was reported by Korf et al. (1987). The sieve fraction of 0.21 mm to 0.30 mm was used during the experimental work. The preparation of the Sn/Li/MgO catalyst was essentially as described by Korf et al. (1989) and the particles were sieved to a size ranging from 0.21 mm to 0.25 mm.

2.5.1.1 Catalyst characterisation

The elemental composition of the catalysts was determined using the Inductively Coupled Plasma technique (ICP) by Tauw Infra Consult b.v. in Deventer (NL). Elementary carbon analysis was performed by Caleb Brett Nederland b.v. in Hoogvliet (NL). The results of these analyses are shown in Table 2.3. The elemental composition of α-Al₂O₃, used as inert packing material, was determined by means of the ICP technique and the results are incorporated in Table 2.5.

The elemental analysis shows that the Li/MgO contains 3.7 wt. % Li, while Li/Sn/MgO contains 4.6 wt. % Li and 3.2 wt. % Sn. The Sn/Li/MgO catalyst was also analysed after the experimental work and the weight percentages Li and Sn amounted to 4.4 and 3.1. These results show no loss of lithium and/or tin during the experimental work.

Couwenberg (1995) carried out XRD measurements on a series of catalysts, among which fresh Li/MgO and Sn/Li/MgO. In the fresh Li/MgO catalyst two crystalline phases were detected: Li₂CO₃ and MgO. In the fresh Sn/Li/MgO catalyst also the same phases MgO and Li₂CO₃ could be detected only. No indications were found for the existence of a Li₂SnMg₃O₆ phase, as suggested by van Keulen et al. (1992), probably due to the low amount of tin in the catalyst. The fresh Li/MgO catalyst probably consists of sintered clusters of MgO crystals, with an average diameter of approximately 1.5 μm. Between these crystals a layer of the Li₂CO₃ phase is present.

The BET surface area was determined using krypton as adsorbent, due to the low surface area of the catalysts. The measurements were performed at the University of Trondheim (Norway) and the results are shown in Table 2.4. The porosity of Li/MgO and Li/Sn/MgO was measured using mercury porosimetry and the results are also shown in Table 2.4.
Experimental set-up and procedures

Table 2.3: Elemental composition of the MgO based catalysts.

<table>
<thead>
<tr>
<th>element</th>
<th>fresh MgO</th>
<th>fresh Li/MgO</th>
<th>fresh Sn/Li/MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>13</td>
<td>3.7 $10^4$</td>
<td>4.6 $10^4$</td>
</tr>
<tr>
<td>Sn</td>
<td>&lt; 50</td>
<td>&lt; 50</td>
<td>3.2 $10^4$</td>
</tr>
<tr>
<td>Mg</td>
<td>54.0 $10^4$</td>
<td>53.0 $10^4$</td>
<td>47.0 $10^4$</td>
</tr>
<tr>
<td>Cu</td>
<td>90</td>
<td>9</td>
<td>21</td>
</tr>
<tr>
<td>Fe</td>
<td>960</td>
<td>66</td>
<td>100</td>
</tr>
<tr>
<td>K</td>
<td>300</td>
<td>71</td>
<td>100</td>
</tr>
<tr>
<td>Na</td>
<td>300</td>
<td>280</td>
<td>430</td>
</tr>
<tr>
<td>Ca</td>
<td>3950</td>
<td>1860</td>
<td>1300</td>
</tr>
<tr>
<td>C</td>
<td>245</td>
<td>-</td>
<td>3240</td>
</tr>
<tr>
<td>Si</td>
<td>1000</td>
<td>600</td>
<td>2300</td>
</tr>
<tr>
<td>Pb</td>
<td>29</td>
<td>18</td>
<td>17</td>
</tr>
<tr>
<td>Zn</td>
<td>42</td>
<td>27</td>
<td>30</td>
</tr>
<tr>
<td>S</td>
<td>2800</td>
<td>1700</td>
<td>2000</td>
</tr>
<tr>
<td>Ni</td>
<td>250</td>
<td>32</td>
<td>75</td>
</tr>
</tbody>
</table>

Table 2.4: BET surface area and porosity of the MgO based catalyst.

<table>
<thead>
<tr>
<th></th>
<th>MgO</th>
<th>Li/MgO</th>
<th>Sn/Li/MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area</td>
<td>25.6</td>
<td>0.6</td>
<td>2.1</td>
</tr>
<tr>
<td>/ m$^2$ g$^{-1}$</td>
<td>± 0.7</td>
<td>± 0.3</td>
<td>± 0.3</td>
</tr>
<tr>
<td>Porosity</td>
<td></td>
<td>0.29</td>
<td>0.21</td>
</tr>
<tr>
<td>/ m$_g^3$ m$_c^{-3}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.5.1.2 Catalyst pretreatment

The catalyst was pretreated, because the state of the catalyst is not stable at high temperatures and a pressure of $10^{-5}$ Pa, due to the desorption of large amounts of carbon dioxide from the catalyst. The pretreatment was carried out in-situ at a temperature of 1073 K with a flow of oxygen and argon (10 vol. %),
amounting to $10^6$ moles per second. In the case of Li/MgO and Sn/Li/MgO desorption of carbon dioxide was observed during the pretreatment. Figure 2.8 shows the intensities of argon, oxygen and carbon dioxide as a function of time during the pretreatment of Sn/Li/MgO. The carbon dioxide signal decreases continuously until the desorption of CO$_2$ is negligible. At this point the pretreatment was stopped and this state of the catalyst was ensured to be reproducible. For Sn/Li/MgO the pretreatment took eight hours for the largest catalyst loading. Desorption of CO$_2$ was also observed for Li/MgO and the pretreatment procedure was carried out in a similar way as for Sn/Li/MgO. No desorption of CO$_2$ was observed in the case of MgO and the pretreatment procedure was carried out during a period of two hours. After the pretreatment the catalyst is cooled down to room temperature after which the experimental work is started.

Furthermore, prior to each experiment the catalyst was exposed to a steady flow of oxygen during a period of five minutes. This treatment was carried out at the same temperature as the experiment to follow. After the flow is switched off, the catalyst is maintained at a pressure of $10^{-5}$ Pa during a period of five minutes in order to remove adsorbed oxygen.

![Graph](image)

**Figure 2.8:** Intensities of argon (+), oxygen (□) and carbon dioxide (■) as a function of time during the pretreatment of Sn/Li/MgO with a steady flow of oxygen and argon (10 vol. %) at a temperature of 1073 K.

### 2.5.2 Platinum and rhodium sponge catalysts

The catalysts used in the experiments on the partial oxidation of methane to synthesis gas are platinum and rhodium sponge, supplied by Johnson Matthey. The
purity of both catalysts is 99.9 wt. % and the particle size is between 250 \( \mu m \) and 350 \( \mu m \). The sponge particles are made up of many sintered non-porous spheres with a diameter of approximately 5 \( \mu m \) for platinum and 2 \( \mu m \) for rhodium. Figure 2.9 shows a Scanning Electron Microscopy (SEM) micrograph of a fresh platinum sponge particle.

\[ \text{Figure 2.9: SEM micrograph of a fresh platinum sponge particle.} \]

### 2.5.2.1 Catalyst characterisation

An elemental analysis of the fresh platinum sponge was performed using the Inductive Coupled Plasma (ICP) technique by Tauw Infra Consult b.v. in Deventer (NL) and an elementary carbon analysis by Caleb Brett Nederland b.v. in Hoogvliet (NL). The elemental composition of the fresh rhodium sponge was determined by an Instrumental Neutron Activation Analysis (INAA) at the Netherlands Energy Research Foundation (ECN) in Petten. In Table 2.5 the elemental composition of platinum and rhodium sponge is shown, together with the elemental composition of \( \alpha \)-\( \text{Al}_2\text{O}_3 \). The most important impurities in the platinum sponge are silicon and sodium. In the case of rhodium the amount of silicon could not be determined by INAA. The amount of impurities is low, though for some elements the detection limits are quite high.

The composition of fresh as well as used platinum and rhodium sponge was further determined by X-Ray Photon Spectroscopy (XPS) and Energy Dispersive
A reaction path analysis of the catalytic partial oxidation of methane by transient experiments

Spectrometry (EDS) measurements. XPS provides quantitative information on the composition of the first few atomic layers of the surface, while EDS has a penetration depth of about 1 μm. XPS measurements were carried out at the Department of Catalysis and Inorganic Chemistry, applying a VG Escalab 200 system with a Al Kα source. Electron binding energies ranging from 0 to 1400 eV were scanned. The EDS measurements were performed at the Department of Solid State Chemistry and Material Science.

**Table 2.5: Elemental composition of platinum and rhodium sponge and α-Al₂O₃.**

<table>
<thead>
<tr>
<th>element</th>
<th>fresh Pt sponge</th>
<th>fresh Rh sponge</th>
<th>α-Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg kg⁻¹</td>
<td>mg kg⁻¹</td>
<td>mg kg⁻¹</td>
</tr>
<tr>
<td>B</td>
<td>&lt; 1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>&lt; 10</td>
<td>-</td>
<td>&lt; 10</td>
</tr>
<tr>
<td>Cd</td>
<td>-</td>
<td>&lt; 50</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>1</td>
<td>&lt; 5</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Cr</td>
<td>5</td>
<td>&lt; 80</td>
<td>6</td>
</tr>
<tr>
<td>Fe</td>
<td>49</td>
<td>&lt; 1000</td>
<td>18</td>
</tr>
<tr>
<td>K</td>
<td>&lt; 50</td>
<td>&lt; 50</td>
<td>&lt; 50</td>
</tr>
<tr>
<td>Li</td>
<td>1.7</td>
<td>-</td>
<td>&lt; 0.4</td>
</tr>
<tr>
<td>Na</td>
<td>200</td>
<td>9.7</td>
<td>-</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt; 1</td>
<td>&lt; 1500</td>
<td>55</td>
</tr>
<tr>
<td>P</td>
<td>&lt; 90</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pd</td>
<td>4.7</td>
<td>&lt; 30</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>Pt</td>
<td>1.0 x 10⁶</td>
<td>73</td>
<td>-</td>
</tr>
<tr>
<td>S</td>
<td>&lt; 30</td>
<td>-</td>
<td>350</td>
</tr>
<tr>
<td>Si</td>
<td>1300</td>
<td>-</td>
<td>45</td>
</tr>
<tr>
<td>Sn</td>
<td>&lt; 8</td>
<td>&lt; 2000</td>
<td>&lt; 8</td>
</tr>
<tr>
<td>Ti</td>
<td>5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td>&lt; 1</td>
<td>&lt; 50</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>
Carbon was the only impurity detected by XPS on the fresh and used platinum sponge as well as rhodium sponge. The amount was too low to quantify. For platinum, the binding energy of the C 1s peak was 285.0 eV and that of the Pt 4f7 peak 71.1 eV, which indicates that carbon is present as carbon graphite and platinum in the form of Pt\(^0\). In the case of rhodium, the binding energy of the C 1s peak was 284.6 eV and that of the Rh 3d5/2 peak 307.1 eV, meaning that carbon is present as carbon graphite and rhodium in the form of Rh\(^0\).

EDS measurements did not show any impurities on both fresh and used platinum and rhodium sponge, with a detection limit of approximately 100 ppm. The results of both the XPS and EDS measurements show that during the experimental work no significant amount of nickel and iron, the main components of inconel, from the reactor wall are deposited on the catalyst.

An elementary carbon analysis of the used platinum sponge showed a carbon content of 120 mg kg\(^{-1}\). The elementary carbon was probably formed during reaction of methane with the catalyst, especially when the platinum was completely reduced.

The BET surface area of the catalysts was determined using krypton as adsorbent, because of the low surface area. The measurements were performed at the Laboratorium voor Chemische Technologie, applying a Micromeritics ASAP 2000 set-up. The BET surface area of the fresh platinum sponge amounts to 0.05 m\(^2\) g\(^{-1}\) and for the fresh rhodium sponge to 0.25 m\(^2\) g\(^{-1}\). These surface areas correspond to diameters of the primary non-porous particles forming the porous grain of 5 \(\mu\)m for platinum and 2 \(\mu\)m for rhodium.

The number of platinum and rhodium surface sites was determined in-situ by an oxygen multipulse experiment over a platinum or rhodium surface precovered with carbon monoxide. The carbon dioxide response was measured and the total amount of carbon dioxide is assumed to be identical to the number of surface sites. The multipulse experiments were performed at a temperature of 373 K and at this temperature no desorption of CO occurs on the time scale of the multipulse experiment. Typically, seven pulses of oxygen were introduced in fourteen seconds. Moreover, for platinum an identical procedure was also carried out, using hydrogen instead of carbon monoxide and measuring the water response. Assuming that both procedures result in an identical carbon dioxide and water formation, the calibration factor of water was calculated from the known carbon dioxide calibration factor.

The number of surface atoms per square meter of the Pt(100) crystal plane is \(1.295 \times 10^{19}\), assuming a face centred cubic crystal structure with a lattice constant of 0.393 nm (Smith, 1990). For rhodium, an atomic area of \(7.6 \times 10^{-20} \text{m}^2\) per rhodium atom is reported (Yates, 1967), resulting in \(1.32 \times 10^{19}\) rhodium atoms per square meter. The surface areas of the fresh platinum and rhodium sponge
determined via this procedure amount to 0.046 m$^2$ g$^{-1}$ and 0.27 m$^2$ g$^{-1}$. These values agree well with those determined ex-situ by the BET method.

2.5.2.2 Catalyst pretreatment

The sponge catalyst is pretreated prior to the experimental work in order to remove some impurities from the catalyst and to obtain a reproducible state of the catalyst during the experiments to follow. The most important impurities are carbon, calcium, phosphorous, sulfur, silicon, chlorine and oxygen (Musket et al., 1982). Impurities like sulfur, carbon and phosphorous are removed from the catalyst surface during an oxygen treatment. Volatile components are removed at 10$^{-5}$ Pa and elevated temperature. After the oxygen pretreatment, the catalyst is partly oxidised and is subsequently reduced by hydrogen.

The platinum and rhodium sponge were pretreated at a temperature of 1123 K. Firstly, the catalyst is exposed to a steady flow of oxygen and argon (10 vol. %) amounting to 10$^{-6}$ mol s$^{-1}$ during one hour. After this, the catalyst is kept at a pressure of 10$^{-5}$ Pa during half an hour. Finally, the catalyst is reduced by a steady flow of hydrogen and argon (10 vol. %) amounting to 10$^{-6}$ mol s$^{-1}$ during one hour.

![Graph showing intensities of argon, oxygen, and water during pretreatment](image)

**Figure 2.10**: Intensities of argon (□), oxygen (■) and water (+) during the pretreatment of rhodium sponge with a steady flow of oxygen and argon (10 vol. %) at a temperature of 1123 K.

The intensities of the relevant components during the oxygen and hydrogen treatment at 1123 K are shown in Figure 2.10 and 2.11 as a function of time for
rhodium sponge. The results for platinum sponge are qualitatively identical.

Figure 2.10 shows that the water signal decreases due to the depletion of hydrocarbon fragments at the surface. Simultaneously, the oxygen signal increases for this reason and also due to the decrease in the incorporation of oxygen into the catalyst. During the treatment with hydrogen the catalyst is reduced, which results in the formation of water, see Figure 2.11. After one hour, the formation of water has stopped and the catalyst was completely reduced. This was checked by pulsing of hydrogen over the reduced catalyst, during which no formation of water was observed.

![Graph of intensities of argon (□), hydrogen (■) and water (+) during the pretreatment of rhodium sponge with a steady flow of hydrogen and argon (10 vol. %) at a temperature of 1123 K.](image)

**Figure 2.11: Intensities of argon (□), hydrogen (■) and water (+) during the pretreatment of rhodium sponge with a steady flow of hydrogen and argon (10 vol. %) at a temperature of 1123 K.**

The surface area of the sponge catalysts decreases as a result of the pretreatment. The surface area of the platinum sponge decreases to 0.035 m² g⁻¹ and the surface area of rhodium sponge to 0.23 m² g⁻¹ after the pretreatment. In both cases the surface area remained constant during the experiments to follow.
**Figure 2.12:** SEM micrograph of a fresh rhodium sponge particle.

**Figure 2.13:** SEM micrograph of a pretreated rhodium sponge particle.
Figure 2.12 and 2.13 show a SEM micrograph of a fresh and pretreated rhodium sponge particle. These figures show that sintering has occurred, which is the cause of the decreased surface area.

References

A reaction path analysis of the catalytic partial oxidation of methane by transient experiments

3

THERMODYNAMICS

3.1 Introduction

In order to obtain insight into the thermodynamic stability of the possible species in the systems oxygen/methane, oxygen/platinum and oxygen/rhodium, equilibrium calculations were carried out. The results, presented in section 3.2, predict the relative stability of the reactants and reaction products as a function of temperature and total pressure. Whether possible reactions really occur on a reasonable time scale depends on the reaction kinetics.

3.2 Thermodynamic equilibrium calculations

3.2.1 Introduction

The equilibrium calculations presented for the system oxygen/methane refer to isothermal and isobaric conditions. The calculations were conducted with Ekvi-Calc V1.21, a computer program developed by Svensk Energi Data (Balinge, 1989). Besides the pressure and temperature, also the number of components in the system and the number of each element present in the system are fixed. The method of equilibrium computation involves the minimization of the total Gibb’s energy of this system with the mole fraction of each component as a free parameter, to give a solution constrained by the mass balance conditions. Reviews of the Gibbs energy minimization method of equilibrium calculations are given by van Zeggen and Storey (1970) and Zeleznik and Gordon (1968). In total twenty two gas phase species and one solid phase species are considered in the
calculations, see Appendix 3A. The latter concerns elementary carbon in the form of graphite. The elementary carbon content is expressed as the percentage of methane converted to elementary carbon. The thermodynamic data for the species were taken from the JANAF Thermochemical Tables by Stull and Prophet (1971) and Chase et al. (1974, 1975, 1978, 1982).

The equilibrium calculations on the systems oxygen/platinum and oxygen/rhodium involve the solving of a set of algebraic equations. The temperature and the number of components in the system are fixed. A set of independent reactions is defined, which accounts for the interactions between the components, with a corresponding equilibrium coefficient. The resulting set of algebraic equations is solved with the activities of the gaseous species as the unknown parameters. The results are presented in so called volatility diagrams, which allow a convenient representation of systems involving three gaseous species. Volatility diagrams are isothermal plots, showing the activities of two gaseous species in equilibrium with the condensed phases. The construction and use of this type of diagram is discussed by Lou et al. (1985) and Heuer (1990).

The species considered in the equilibrium calculations are $O_2(g)$, $Pt\,(c)$, $Pt\,(g)$, $PtO\,(c)$, $Pt_2O_4\,(c)$, $PtO_2\,(c)$ and $PtO_2\,(g)$ for the system oxygen/platinum, according to Wagman et al. (1982) and Barin (1993) and $O_2(g)$, $Rh\,(c)$, $Rh\,(g)$, $Rh_2O\,(c)$, $RhO\,(c)$, $Rh_2O_3\,(c)$ and $RhO_2\,(g)$ for the system oxygen/rhodium, according to Alcock and Hooper (1960), Schäfer et al. (1963) and Barin (1993). The data for the equilibrium calculations were taken from Barin (1993) for oxygen/platinum and from Alcock and Hooper (1960), Barin and Knacke (1973), Barin et al. (1977) and Barin (1993) for oxygen/rhodium. Only the results at a temperature of 1000 K are presented here, since this temperature is the most relevant for the present study. For both systems in total fourteen reactions account for the various interactions of the seven gaseous and condensed species. These reactions with their corresponding equilibrium coefficients at 1000 K are shown in Appendix 3B for the system oxygen/platinum and in Appendix 3C for the system oxygen/rhodium.

### 3.2.2 Results for the system oxygen/methane

Equilibrium calculations on the system oxygen/methane were conducted for the temperature range of 300 K to 1500 K at a constant pressure of $10^5$ Pa and four different methane to oxygen feed molar ratios: 0.5, 1, 2 and 3.

In the case of a methane to oxygen feed molar ratio of 0.5 only CO$_2$ and H$_2$O are present at thermodynamic equilibrium between 300 K and 1500 K. The equilibrium composition as a function of temperature at a methane to oxygen feed molar ratio of 1 is shown in Figure 3.1. At temperatures below 400 K only methane, carbon dioxide, water and elementary carbon are present. At 450 K
hydrogen is also present due to a shift of the steam reforming reaction, Equation 3.1, to the right.

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad \Delta_r H_{298}^\circ = 206.17 \text{ kJ mol}^{-1} \quad (3.1) \]

Carbon monoxide is not present at this temperature due to the watergas shift reaction, which equilibrium is on the right, see Equation 3.2.

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad \Delta_r H_{298}^\circ = -41.14 \text{ kJ mol}^{-1} \quad (3.2) \]

At increasing temperature the equilibrium of the carbon dioxide reforming reaction, see Equation 3.3, will shift to the right, resulting in an increase in the carbon monoxide and hydrogen partial pressure.

\[ \text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \quad \Delta_r H_{298}^\circ = 247.31 \text{ kJ mol}^{-1} \quad (3.3) \]

At temperatures above 1100 K the equilibrium of the watergas shift reaction 3.2 will shift to the left, resulting in an increase in the CO and H\text{2}O partial pressure. In this way the hydrogen partial pressure shows a maximum at approximately 1000 K, see Figure 3.1.

The results of the equilibrium calculations at a methane to oxygen feed molar ratio of 2 are presented in Figure 3.2 at a constant pressure of 10\text{5} Pa. As in the

![Figure 3.1: Equilibrium composition as a function of temperature at a methane to oxygen feed molar ratio of 1 and a constant pressure of 10\text{5} Pa. The partial pressure of the gaseous species \text{CH}_4, \text{CO}, \text{H}_2, \text{CO}_2 and \text{H}_2\text{O} is shown on the left vertical axis and the elementary carbon content on the right vertical axis.](image)
case of a molar ratio of 1, at temperatures below 400 K only methane, water, carbon dioxide and elementary carbon are present. At 450 K the hydrogen partial pressure increases due to a shift of equilibrium of both the steam reforming reaction, Equation 3.1, and the watergas shift reaction, Equation 3.2, to the right.

\[ \text{Figure 3.2: Equilibrium composition as a function of temperature at a methane to oxygen feed molar ratio of 2 and a constant pressure of } 10^5 \text{ Pa. The partial pressure of the gaseous species } CH_4, CO, H_2, CO_2 \text{ and } H_2O \text{ is shown on the left vertical axis and the elementary carbon content on the right vertical axis.} \]

At increasing temperature a maximum in the concentration of elementary carbon is observed, due to the endothermicity of the methane dissociation reaction, Equation 3.4, and the carbon dioxide reforming reaction, Equation 3.3, which equilibrium is on the left side at this temperature.

\[ CH_4 \rightarrow C + 2 H_2 \quad \Delta_r H_{298}^0 = 74.87 \text{ kJ mol}^{-1} \quad (3.4) \]

At high temperatures the partial pressures of CO and H\(_2\) increase and from 1300 K onwards only H\(_2\) and CO are present in the molar ratio of 2.

Figure 3.3 shows the equilibrium composition as a function of temperature at a methane to oxygen feed molar ratio of 3 and in this case oxygen is the limiting reactant for the production of synthesis gas. At equilibrium no C\(_2\)-products, e.g. ethane and ethene, are present up to temperatures of 1500 K, but the excess in carbon is present in the form of elementary carbon. From a temperature of 1400 K onwards the partial pressure of carbon monoxide and hydrogen as well as the elementary carbon content remain constant.
Figure 3.3: Equilibrium composition as a function of temperature at a methane to oxygen feed molar ratio of 3 and a constant pressure of $10^5$ Pa. The partial pressure of the gaseous species $\text{CH}_4$, CO, $\text{H}_2$, $\text{CO}_2$ and $\text{H}_2\text{O}$ is shown on the left vertical axis and the elementary carbon content on the right vertical axis.

Figure 3.4: Equilibrium composition as a function of temperature at a methane to oxygen feed molar ratio of 2 and a constant pressure of 100 bar. The partial pressure of the gaseous species $\text{CH}_4$, CO, $\text{H}_2$, $\text{CO}_2$ and $\text{H}_2\text{O}$ is shown on the left vertical axis and the elementary carbon content on the right vertical axis.
Most industrial processes are carried out at elevated pressure to reduce the equipment size and therefore the effect of the total pressure on the equilibrium composition is studied. Figure 3.4 shows the results at a methane to oxygen molar ratio of 2 and a total pressure of 100 bar. Comparison of the results at a total pressure of $10^5$ Pa, Figure 3.2, and 100 Pa, Figure 3.4, shows that the maximum in the elementary carbon content is much less pronounced at 100 bar. The temperature at which only hydrogen and carbon monoxide are present at equilibrium amounts to 1300 K at $10^5$ Pa, but this temperature is much higher in the case of 100 bar, since at 1700 K still methane and water are present at equilibrium.

### 3.2.3 Results for the system oxygen/platinum and oxygen/rhodium

The volatility diagram for the system oxygen/platinum at a temperature of 1000 K is shown in Figure 3.5. The volatility diagram consists of four fields assigned to Pt$_{(c)}$, PtO$_{(c)}$, PtO$_2$(c) and a gas phase, consisting of PtO$_2$(g), Pt$_{(g)}$ and O$_2$(g). The equilibrium composition of the gas phase is ruled by the equilibrium constant of the following reaction, Equation 3.5:

$$PtO_2(g) \rightleftharpoons Pt(g) + O_2(g)$$

At a given activity of O$_2$(g) and Pt$_{(g)}$, the activity of PtO$_2$(g) is fixed by the equilibrium of Equation 3.5. The lines A to B correspond to an equilibrium between the gas phase and one or more condensed phases. The triple points T and S, Figure 3.5, represent the points where three phases are in equilibrium. For example, in triple point T the condensed phases Pt$_{(c)}$ and PtO$_{(c)}$ and the gas phase are in equilibrium, leaving the temperature as the only degree of freedom.

The minimum activity of oxygen necessary for the formation of PtO$_2$(c) corresponds to the triple point S and amounts to $6.31 \times 10^7$ Pa. At increasing temperature, the field corresponding to condensed PtO$_2$ becomes smaller.

The volatility diagram for the system oxygen/rhodium at a temperature of 1000 K is shown in Figure 3.6. As in the case of platinum, four fields can be assigned, corresponding to Rh$_{(c)}$, Rh$_2$O$_{(c)}$, Rh$_2$O$_3$(c) and a gas phase. The latter consists of RhO$_2$(g), Rh$_{(g)}$ and O$_2$(g). At a given activity of O$_2$(g) and Rh$_{(g)}$, the activity of RhO$_2$(g) is fixed by the equilibrium of the reaction given by Equation 3.6.

$$RhO_2(g) \rightleftharpoons Rh(g) + O_2(g)$$

At a given activity of O$_2$(g) and Rh$_{(g)}$, the activity of RhO$_2$(g) is fixed by the equilibrium of the reaction given by Equation 3.6.
Figure 3.5: Volatility diagram of the system oxygen/platinum at a temperature of 1000 K and isobaric conditions; logarithmic value of the PtO_x activity versus the logarithmic value of the dioxygen activity.

Figure 3.6: Volatility diagram of the system oxygen/rhodium at a temperature of 1000 K and isobaric conditions; logarithmic value of the RhO_x activity versus the logarithmic value of the dioxygen activity.
The lines A to B, Figure 3.6, correspond to the equilibrium between the gas phase and one or more condensed phases. The minimum activity of oxygen necessary for the formation of Rh$_2$O$_3$, corresponding to triple point S, amounts to 250 Pa. This value is much lower than the oxygen activity necessary for oxide formation in the case of platinum. The field corresponding to Rh$_2$O$_3$ becomes smaller at increasing temperature.

3.3 Conclusions

For methane and oxygen the gas mixture at equilibrium solely consists of carbon dioxide and water at a methane to oxygen feed molar ratio of 0.5. At ratios of 1, 2 and 3 the components methane, carbon dioxide, water and elementary carbon are present at low temperatures. At increasing temperature also carbon monoxide and hydrogen are present at equilibrium. The composition at high temperatures depends on the methane to oxygen feed molar ratio. At a ratio of 1 hydrogen, carbon monoxide, water and carbon dioxide are present, while at a ratio of 2 the gas mixture solely consists of hydrogen and carbon monoxide. Besides CO and H$_2$, also elementary carbon is present at a ratio of 3 and high temperatures. Ethane and ethene are not present at equilibrium up to a methane to oxygen feed molar ratio of 3. The temperature at which the gas mixture solely consists of hydrogen and carbon monoxide at a feed molar ratio of 2 increases towards a higher value at increasing total pressure.

Equilibrium calculations have shown that formation of a platinum oxide phase is expected at a much higher oxygen activity when compared to the activity necessary for formation of a rhodium oxide phase. For both metals two gaseous species can be formed at a temperature of 1000 K.

References


Appendix 3A: Species considered in the equilibrium calculations on the system oxygen/methane.

The following species were considered in the equilibrium calculations on the system oxygen/methane:

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>carbon</td>
<td>C(_{\text{g}})</td>
</tr>
<tr>
<td>2</td>
<td>graphite</td>
<td>C(_{\text{s}})</td>
</tr>
<tr>
<td>3</td>
<td>methyldene radical</td>
<td>CH(_2^+)</td>
</tr>
<tr>
<td>4</td>
<td>methylene radical</td>
<td>CH(_2^+)</td>
</tr>
<tr>
<td>5</td>
<td>methyl radical</td>
<td>CH(_3^+)</td>
</tr>
<tr>
<td>6</td>
<td>methane</td>
<td>CH(_4)</td>
</tr>
<tr>
<td>7</td>
<td>ethyne</td>
<td>C(_2)H(_2)</td>
</tr>
<tr>
<td>8</td>
<td>ethene</td>
<td>C(_2)H(_4)</td>
</tr>
<tr>
<td>9</td>
<td>ethane</td>
<td>C(_2)H(_6)</td>
</tr>
<tr>
<td>10</td>
<td>oxygen radical</td>
<td>O(^+)</td>
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<td>O(_2)</td>
</tr>
<tr>
<td>12</td>
<td>hydroxyl radical</td>
<td>OH(^+)</td>
</tr>
<tr>
<td>13</td>
<td>hydrogen radical</td>
<td>H(^+)</td>
</tr>
<tr>
<td>14</td>
<td>hydrogen</td>
<td>H(_2)</td>
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<tr>
<td>15</td>
<td>water</td>
<td>H(_2)O</td>
</tr>
<tr>
<td>16</td>
<td>hydrogen peroxyde</td>
<td>H(_2)O(_2)</td>
</tr>
<tr>
<td>17</td>
<td>hydrogen peroxyde radical</td>
<td>H(_2)O(_2^+)</td>
</tr>
<tr>
<td>18</td>
<td>carbon monoxide</td>
<td>CO</td>
</tr>
<tr>
<td>19</td>
<td>carbon dioxide</td>
<td>CO(_2)</td>
</tr>
<tr>
<td>20</td>
<td>formyl radical</td>
<td>HCO(^+)</td>
</tr>
<tr>
<td>21</td>
<td>methanal</td>
<td>HCHO</td>
</tr>
<tr>
<td>22</td>
<td>methanol</td>
<td>CH(_3)OH</td>
</tr>
<tr>
<td>23</td>
<td>ethanal</td>
<td>CH(_3)CHO</td>
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Appendix 3B: Reactions and corresponding logarithmic values of the equilibrium constant at 1000 K for the reactions in the system oxygen/platinum.

Activities are defined with respect to a standard pressure of 1 bar.

<table>
<thead>
<tr>
<th>Equation number</th>
<th>Overall reaction equation</th>
<th>Log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(2 \text{Pt}_\text{(c)} + \text{O}_2\text{(g)} \rightleftharpoons 2 \text{PtO}_2\text{(c)})</td>
<td>-1.28</td>
</tr>
<tr>
<td>2</td>
<td>(\frac{3}{2} \text{Pt}_\text{(c)} + \text{O}_2\text{(g)} \rightleftharpoons \frac{1}{2} \text{Pt}_3\text{O}_4\text{(c)})</td>
<td>-2.21</td>
</tr>
<tr>
<td>3</td>
<td>(\text{Pt}_\text{(c)} + \text{O}_2\text{(g)} \rightleftharpoons \text{PtO}_2\text{(c)})</td>
<td>-8.45</td>
</tr>
<tr>
<td>4</td>
<td>(6 \text{PtO}_2\text{(c)} + \text{O}_2\text{(g)} \rightleftharpoons 2 \text{Pt}_3\text{O}_4\text{(g)})</td>
<td>-4.98</td>
</tr>
<tr>
<td>5</td>
<td>(2 \text{PtO}_2\text{(c)} + \text{O}_2\text{(g)} \rightleftharpoons 2 \text{PtO}_2\text{(g)})</td>
<td>-15.63</td>
</tr>
<tr>
<td>6</td>
<td>(\text{Pt}_3\text{O}_4\text{(c)} + \text{O}_2\text{(g)} \rightleftharpoons 3 \text{PtO}_2\text{(g)})</td>
<td>-20.95</td>
</tr>
<tr>
<td>7</td>
<td>(\text{Pt}<em>\text{(c)} \rightleftharpoons \text{Pt}</em>\text{(g)})</td>
<td>-21.64</td>
</tr>
<tr>
<td>8</td>
<td>(2 \text{PtO}<em>2\text{(c)} \rightleftharpoons 2 \text{Pt}</em>\text{(g)} + \text{O}_2\text{(g)})</td>
<td>-42.00</td>
</tr>
<tr>
<td>9</td>
<td>(\frac{1}{2} \text{Pt}_3\text{O}<em>4\text{(c)} \rightleftharpoons \frac{3}{2} \text{Pt}</em>\text{(g)} + \text{O}_2\text{(g)})</td>
<td>-30.26</td>
</tr>
<tr>
<td>10</td>
<td>(\text{Pt}_\text{(c)} + \text{O}_2\text{(g)} \rightleftharpoons \text{PtO}_2\text{(c)})</td>
<td>-2.07</td>
</tr>
<tr>
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<td>(2 \text{PtO}_2\text{(c)} + \text{O}_2\text{(g)} \rightleftharpoons 2 \text{PtO}_2\text{(c)})</td>
<td>-2.85</td>
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<td>12</td>
<td>(\text{Pt}_3\text{O}_4\text{(c)} + \text{O}_2\text{(g)} \rightleftharpoons 3 \text{PtO}_2\text{(c)})</td>
<td>-1.79</td>
</tr>
<tr>
<td>13</td>
<td>(\text{PtO}_2\text{(c)} \rightleftharpoons \text{PtO}_2\text{(g)})</td>
<td>-6.39</td>
</tr>
<tr>
<td>14</td>
<td>(\text{PtO}<em>3\text{(c)} \rightleftharpoons \text{Pt}</em>\text{(g)} + \frac{3}{2} \text{O}_2\text{(g)})</td>
<td>-19.58</td>
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</table>
Appendix 3C: Reactions and corresponding logarithmic values of the equilibrium constant at 1000 K for the reactions in the system oxygen/rhodium.

Activities are defined with respect to a standard pressure of 1 bar.

<table>
<thead>
<tr>
<th>Equation number</th>
<th>Overall reaction equation</th>
<th>Log K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4 Rh(<em>{(c)}) + O(</em>{2(g)}) ↔ 2 Rh(<em>{2}O(</em>{(c)})</td>
<td>5.08</td>
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<tr>
<td>2</td>
<td>2 Rh(<em>{(c)}) + O(</em>{2(g)}) ↔ 2 RhO(_{(c)})</td>
<td>1.63</td>
</tr>
<tr>
<td>3</td>
<td>4/3 Rh(<em>{(c)}) + O(</em>{2(g)}) ↔ 2/3 Rh(<em>{2}O</em>{3(c)})</td>
<td>3.43</td>
</tr>
<tr>
<td>4</td>
<td>Rh(<em>{(c)}) + O(</em>{2(g)}) ↔ RhO(_{2(g)})</td>
<td>-8.79</td>
</tr>
<tr>
<td>5</td>
<td>2 Rh(<em>{2}O(</em>{(c)}) + O(<em>{2(g)}) ↔ 4 RhO(</em>{(c)})</td>
<td>-1.82</td>
</tr>
<tr>
<td>6</td>
<td>Rh(<em>{2}O(</em>{(c)}) + O(<em>{2(g)}) ↔ Rh(</em>{2}O_{3(c)})</td>
<td>2.60</td>
</tr>
<tr>
<td>7</td>
<td>2/3 Rh(<em>{2}O(</em>{(c)}) + O(<em>{2(g)}) ↔ 4/3 RhO(</em>{2(g)})</td>
<td>-13.41</td>
</tr>
<tr>
<td>8</td>
<td>4 RhO(<em>{(c)}) + O(</em>{2(g)}) ↔ 2 Rh(<em>{2}O</em>{3(c)})</td>
<td>7.03</td>
</tr>
<tr>
<td>9</td>
<td>2 RhO(<em>{(c)}) + O(</em>{2(g)}) ↔ 2 RhO(_{2(g)})</td>
<td>-19.20</td>
</tr>
<tr>
<td>10</td>
<td>2 Rh(<em>{2}O</em>{3(c)}) + O(<em>{2(g)}) ↔ 4 RhO(</em>{2(g)})</td>
<td>-45.43</td>
</tr>
<tr>
<td>11</td>
<td>Rh(<em>{(c)}) ↔ Rh(</em>{(g)})</td>
<td>-20.95</td>
</tr>
<tr>
<td>12</td>
<td>2 Rh(<em>{2}O(</em>{(c)}) ↔ 4 Rh(<em>{(g)}) + O(</em>{2(g)})</td>
<td>-88.89</td>
</tr>
<tr>
<td>13</td>
<td>2 RhO(<em>{(c)}) ↔ 2 Rh(</em>{(g)}) + O(_{2(g)})</td>
<td>-43.53</td>
</tr>
<tr>
<td>14</td>
<td>2/3 Rh(<em>{2}O</em>{3(c)}) ↔ 4/3 Rh(<em>{(g)}) + O(</em>{2(g)})</td>
<td>-31.36</td>
</tr>
</tbody>
</table>
4

REACTION NETWORK FOR THE OXIDATIVE COUPLING OF METHANE OVER TIN PROMOTED LITHIUM ON MAGNESIUM OXIDE

4.1 Introduction

The elementary reactions in the catalytic oxidative coupling of methane are not completely understood yet, especially those leading to side products. Methyl radicals are produced at the catalyst surface and react further in the gas phase (Driscoll et al., 1985A; Driscoll et al., 1985B; Campbell et al., 1987; Campbell et al., 1988). Ethane is produced to a large extent in the gas phase as primary C₂ product, which is subsequently dehydrogenated to ethene (Ito et al., 1985; Nelson et al., 1988). Parallel reaction paths for COₓ formation have been proposed on PbO/Al₂O₃ (Hinsen et al., 1985), Li/MgO (Peil et al., 1991; Nelson et al., 1989), Na/MnOₓ/SiO₂ (Burch et al., 1990) and NaOH/CaO (Follmer et al., 1989; Lehmann and Baerns, 1992) as catalyst. Oxidation of methyl radicals was concluded to be the primary source for COₓ at temperatures below 973 K using a Li/MgO catalyst (Ito et al., 1985). However, C₂ product oxidation is also considered an important source for COₓ in the case of Li/MgO at temperatures higher than 993 K (Nelson and Cant, 1990; Roos et al., 1989).

The reactivity of lattice oxygen versus adsorbed oxygen is also a matter of debate. In the case of PbO lattice oxygen was found to be the active species for C₂ product formation, whereas adsorbed oxygen was claimed to be active for the COₓ formation (Asami et al., 1987).

The objective of the work presented in this chapter is to investigate the reaction network of the oxidative coupling of methane over Sn/Li/MgO. By varying
the amount of admitted molecules in a single TAP pulse the potential contribution of gas phase reactions, i.e. not involving the catalyst surface, can be evaluated. Pulse intensities of \(10^{15}-10^{16}\) molecules correspond to a pressure above the catalyst surface of 100 Pa, which is low enough to suppress gas phase reactions at typical coupling temperatures. This holds in particular for the coupling of methyl radicals which is far in the low pressure regime according to the unimolecular rate theory of Rice-Ramsperger-Kassel-Marcus (Robinson and Holbrook, 1972), since calculations based on literature pressure fall-off data (Chen et al., 1994) showed that in this regime the rate coefficient for coupling is proportional to the total pressure and that coupling can indeed occur to a significant extent from pulse intensities of \(10^{17}\) molecules on, in this paper referred to as high pressure regime. In the TAP set-up the pulse intensities can be conveniently varied from \(10^{15}\) to \(10^{17}\) molecules. The corresponding changes in the product distribution can be assigned to the appearance of gas phase reactions.

4.2 Experimental procedures and definitions

Non porous \(\alpha\)-alumina was used as inert packing material in the sieve fraction of 0.21 to 0.25 mm. Blank pulse experiments of methane as well as ethane with oxygen over \(\alpha\)-alumina at a temperature of 973 K in the high pressure regime showed a conversion of two percent, which is negligible compared to conversions obtained in the presence of the catalyst. The microreactor was charged with 0.1 to 0.5 g of Sn/Li/MgO and packed with inert at each end. The catalyst was pretreated as described in section 2.5.1.2. Furthermore, prior to each experiment the catalyst was exposed to a steady flow of oxygen during five minutes after which adsorbed oxygen was removed by maintaining a vacuum of \(10^{-5}\) Pa during five minutes. Argon was always added to the admitted gases as reference component for determination of the pulse size and calculation of the conversion.

The experiments were carried out in the temperature range of 373 K to 1073 K and pulse intensities in the range of \(10^{15}\) to \(10^{17}\) molecules per pulse. It was not possible to detect carbon dioxide quantitatively at the reactor outlet due to its strong adsorption on the catalyst surface, as shown by pulse experiments of carbon dioxide up to a temperature of 973 K, in which no breakthrough was observed. Therefore carbon dioxide formation was deduced from the carbon balance, although methyl radicals could not be accounted for quantitatively. However, the ratio of the peak area of the response of AMU 15 and 16 was calculated and an increase compared to the ratio given by the fragmentation pattern of methane at equal conditions is an indication for formation of methyl radicals, as proposed by Buyevskaya et al., 1994.
For each experiment the conversion and yields were calculated according to the following equations:

\[ X_{CH_4} = \frac{n_{\text{in,CH}_4} - n_{\text{out,CH}_4}}{n_{\text{in,CH}_4}} \] \hspace{2cm} (4.1)

\[ Y_{C_2H_6} = \frac{2n_{\text{out,C}_2\text{H}_6}}{n_{\text{in,CH}_4}} \] \hspace{2cm} (4.2)

\[ Y_{CO} = \frac{n_{\text{out,CO}}}{n_{\text{in,CH}_4}} \] \hspace{2cm} (4.3)

\[ Y_{CO_2} = \frac{n_{\text{in,CH}_4} - n_{\text{out,CH}_4} - n_{\text{out,CO}} - 2n_{\text{out,C}_2\text{H}_6}}{n_{\text{in,CH}_4}} \] \hspace{2cm} (4.4)

where \( n \) is the total number of moles (mol), \( X \) is the conversion (mol mol\(^{-1}\)) and \( Y \) is the yield (mol mol\(^{-1}\)). The subscript "in" means introduced into the reactor and the subscript "out" means detected at the reactor outlet.

4.3 Results and discussion

4.3.1 Adsorption of oxygen

Adsorption of oxygen was studied with multipulse experiments over 0.1 g of catalyst at a temperature of 973 K. The surface area of the oxygen responses increases for the first pulses to remain subsequently constant. The initial lower oxygen signals are due to oxygen interacting strongly with the catalyst. It takes approximately three minutes for this oxygen to desorb completely which is too long to cause a signal above the noise level. The individual responses are all broadened, with respect to a blank experiment, which points to adsorption of a second type of oxygen species. The time scale for desorption of this adsorbed oxygen amounts to four seconds. The quantity of strongly interacting oxygen, expressed as a percentage of the theoretical amount of surface oxygen, amounts to 6.9 % for Sn/Li/MgO compared to 0.1 % for MgO. The increased capacity for strongly interacting oxygen of Sn/Li/MgO compared to MgO may be due to a Li\(_2\)CO\(_3\) phase, which may still be present under vacuum conditions as shown by XPS studies (Peng et al., 1990).
4.3.2 Formation of methyl radicals

Pulse experiments with methane alone were performed over 0.4 g of catalyst, in the low as well as the high pressure regime. In the latter case the ratio of admitted methane to the theoretical number of surface oxygen atoms is 0.05. In the low pressure regime the methane conversion amounted to 7 % at 833 K and increased to 61 % at 973 K. Formation of methyl radicals was observed, not accompanied by any coupling products or carbon monoxide formation. In the high pressure regime the methane conversion amounted to 3 % at 833 K and 37 % at 973 K. Methyl radicals now were detected in a much lower amount compared to the previous experiments. Formation of ethane and carbon monoxide was observed. Ethene was not produced. In both experiments large amounts of carbon dioxide were produced as derived from the carbon balance. These results confirm the generally accepted point of view that ethane is produced in the gas phase by coupling of two methyl radicals.

4.3.3 Conversion of methane and oxygen

Methane and oxygen were pulsed simultaneously over 0.5 g of catalyst in the high pressure regime at a temperature of 973 K. The ratio was 0.6 to ensure complete reoxidation of the catalyst. The conversion of methane amounted to 60 %. No breakthrough of oxygen was observed, as expected from the observations reported in section 4.3.1. The formed reaction products were methyl radicals, ethane, carbon monoxide and carbon dioxide. No formation of ethene occurred. The normalised responses of ethane and carbon monoxide, shown in Figure 4.1, indicate that carbon monoxide is a product from ethane, since the combined response is observed later when compared to the response of ethane alone.

The influence of adsorbed oxygen on the conversion of methane was investigated by an alternating pulse experiment, pulsing oxygen first and next methane. Eight different time intervals between the pulses were applied, varying from zero, i.e. simultaneous pulsing, to 10 s. The corresponding conversion of methane decreased from 60 % to 44 %. In the latter case the conversion was equal to that obtained when pulsing methane alone. No formation of ethene occurred. The yield of ethane and carbon monoxide was equal at all time intervals, meaning that the change of the methane conversion in the presence of adsorbed oxygen is solely due to carbon dioxide formation.

These results indicate that in parallel to the formation of ethane, methane is directly converted to carbon dioxide by involvement of adsorbed oxygen. Furthermore, carbon monoxide is not a primary reaction product, conform the results of Tung et al. (1992) for Li/MgO.
Figure 4.1: Response of ethane (x 5.9) (A) and carbon monoxide plus ethane (B) when pulsing methane and oxygen simultaneously over Sn/Li/MgO in the high pressure regime at a temperature of 973 K.

In order to verify the direct conversion of methane to carbon dioxide, methane and oxygen were pulsed simultaneously in the high pressure regime over MgO, since in this particular case it is possible to detect carbon dioxide quantitatively. The methane to oxygen ratio was 0.4 and the conversion of methane was 77% at a temperature of 1023 K.

Figure 4.2: Response of ethane (x 16.7) (A), carbon monoxide plus ethane (B) and carbon dioxide (x 2.4) (C) when pulsing methane and oxygen simultaneously over MgO in the high pressure regime at a temperature of 1023 K.
The normalised responses of ethane, carbon monoxide plus ethane as well as carbon dioxide are shown in Figure 4.2. Carbon dioxide is a primary reaction product, since the response is observed prior to that of ethane, as well as a secondary reaction product produced from carbon monoxide. The latter is only produced from ethane, since the combined response of carbon monoxide plus ethane is observed later than the response of ethane alone.

4.3.4 Conversion of ethane and oxygen

The reaction paths of ethane were investigated with pulse experiments over 0.1 g of catalyst in the low and in the high pressure regime, using ethane alone as well as simultaneously with oxygen. In all cases the main reaction product was carbon dioxide. The normalised responses of ethane, the \( C_2 \) products as well as carbon monoxide plus the \( C_2 \) products when pulsing ethane and oxygen simultaneously at a ratio of 0.4 in the high pressure regime at 1073 K are shown in Figure 4.3. The conversion of ethane amounted to 81%. Carbon monoxide was formed directly from ethane as response C deviates from the ethane response before response B does. The small but reproducible deviation of response B from the ethane response can be attributed to the formation of ethene. Pulsing of ethane and oxygen simultaneously in the low pressure regime resulted in formation of carbon monoxide. However, ethene was not produced since the normalised responses of ethane and the \( C_2 \) products were completely identical. Ethene was not produced either when pulsing ethane alone in the low or high pressure regime.

\[ \text{Figure 4.3: Response of ethane (x 6.3) (A), C}_2\text{ products (x 4.3) (B) and carbon monoxide plus C}_2\text{ products (C) when pulsing ethane and oxygen simultaneously over Sn/Li/MgO in the high pressure regime at a temperature of 1073 K.} \]
These results demonstrate that ethane is converted to carbon monoxide by interaction with the surface. Furthermore, formation of ethene takes place as a gas phase reaction in which dioxygen is involved. A possible mechanism consists of the generation of ethyl radicals on the surface, which react with dioxygen towards ethene, as proposed by Morales and Lunsford (1989) for Li/MgO. The direct decomposition of ethyl radicals towards ethene (Chen et al., 1991) can be ruled out, even in the high pressure regime.

As for methane, the influence of adsorbed oxygen on the conversion of ethane was investigated by an alternating pulse experiment of oxygen followed by methane over 0.4 g of catalyst at a temperature of 973 K and a ethane to oxygen ratio of 0.4. Six different time intervals between the pulses were applied varying from zero to 5 s. The corresponding conversion of ethane decreased from 69 % to 57 %, the latter being equal to that obtained when pulsing ethane alone. The yield of carbon dioxide and in this case also of carbon monoxide decreased accordingly. The produced amount of ethene was already low in the case of simultaneous pulsing and vanishes completely at the smallest time interval which was applied, i.e. 20 ms. These results show that both lattice and adsorbed oxygen are involved in the non selective reaction path of ethane. There is no reason to exclude such a mechanism for methane. Since carbon monoxide is not directly produced from methane there are no direct indications in the latter case, however. The involvement of lattice oxygen in the reaction paths of the oxidative coupling of methane is further addressed in Chapter 5.

4.3.5 Conversion of ethene and carbon monoxide

Ethene alone was pulsed in the low and high pressure regime over 0.4 g of catalyst as well as simultaneous with oxygen at a ratio of 0.6 and a temperature of 973 K. Carbon monoxide as well as carbon dioxide was always formed. Carbon monoxide was pulsed in the low pressure regime. Its conversion starts at a temperature of 523 K and increases to 95 % at 723 K.

4.4 Conclusions

The oxidative coupling of methane over Sn/Li/MgO in the presence of both methane and oxygen at a temperature of 973 K proceeds as follows. Methyl radicals are produced at the surface and combine in the gas phase to form ethane. Ethene is produced from ethane via a gas phase reaction in which dioxygen is involved. This reaction may involve ethyl radicals produced by the catalyst. Both ethane and ethene are oxidised to carbon monoxide at the surface. Carbon monoxide is oxidised to carbon dioxide by interaction with the surface. In parallel
to the formation of ethane, methane is directly converted to carbon dioxide by involvement of adsorbed oxygen. It seems likely that the latter also proceeds via lattice oxygen. Both lattice and adsorbed oxygen are involved in the non selective reaction path of ethane.

References


A reaction path analysis of the catalytic partial oxidation of methane by transient experiments
5

OXYGEN PATHWAYS IN THE OXIDATIVE COUPLING OF METHANE OVER MAGNESIUM OXIDE BASED CATALYSTS

5.1 Introduction

The oxidative coupling of methane aims at the production of ethane and ethene, abbreviated as C₂ products, at temperatures between 900 and 1200 K and pressures between 100 and 1000 kPa.

Keller and Bhasin (1982) were among the first to report formation of C₂ products when feeding in an alternating way methane and air to metal oxides supported on γ-Al₂O₃. Production of C₂ products was reported for a supported lead oxide catalyst by Hinsen and Baarns (1983) as well as for Li/MgO by Ito and Lunsford (1985) when cofeeding methane and oxygen.

In the oxidative coupling of methane the production of methyl radicals proceeds via methane activation at the catalyst surface (Ito et al., 1985; Driscoll and Lunsford, 1985; Campbell et al., 1987; Campbell and Lunsford, 1988). Non-selective reactions are catalysed by the surface as well, leading to the formation of COₓ. The active centers for methyl radical formation in the case of Li/MgO are considered to be Li⁺O⁻ centers, as identified by EPR (Ito and Lunsford, 1985; Ito et al., 1985; Driscoll et al., 1985; Lin et al., 1987), or O⁻ ions which are in equilibrium with these centers (Wang and Lunsford, 1986). The Li⁺O⁻ centers are formed by the substitution of Mg by Li into the MgO lattice which is possible since the respective ionic radii are nearly equivalent. Besides O⁻ anions also other reactive forms of oxygen were mentioned in the oxidative coupling of methane e.g. the superoxide anion O₂⁻ (Lunsford, 1990; Lin et al., 1986), the oxide anion O²⁻
A reaction path analysis of the catalytic partial oxidation of methane by transient experiments

(Driscoll et al., 1987; Che and Tench, 1982; Sokolovskii et al., 1989), the peroxyde anion \( \text{O}_2^{2-} \) (Otsuka et al., 1987; Kharas and Lunsford, 1989; Otsuka et al., 1990; Sinev et al., 1986) and the ozonide anion \( \text{O}_3^- \) (Lunsford, 1990).

The oxidative coupling over MgO and Li/MgO (Peil et al., 1989; Peil et al., 1991; Nibbelke et al., 1995) and Sn/Li/MgO (Nibbelke et al., 1995) was studied using steady-state isotopic transient kinetic analysis. It was concluded that oxygen interacts strongly with the surface by dissociative reversible adsorption. Both surface and bulk lattice oxygen participate in the reaction. The promotion with lithium and even more with tin increases the mobility of oxygen in the bulk and the amount of exchangeable oxygen per unit BET surface area. Cant et al. (1990) studied the rates of oxygen isotope exchange processes over Li/MgO using \(^{16}\text{O}_2/^{18}\text{O}_2\) mixtures at temperatures of 973 K up to 1023 K. It was concluded that the exchange occurs via oxygen present as \( \text{Li}_2\text{O} \), which also is likely to be involved in the activation of methane. An increase in the exchange between gas phase and lattice oxygen is also reported for Sr promoted \( \text{La}_2\text{O}_3 \) (Kalenik and Wolf, 1991; Kalenik and Wolf, 1992). The mobility of lattice oxygen increases and oxygen vacancies are created in the structure of \( \text{La}_2\text{O}_3 \). Buyevskaya et al. (1994B) studied the interaction of oxygen with catalytic surfaces of MgO, \( \text{Sm}_2\text{O}_3 \) (5 %)/MgO and \( \text{Sm}_2\text{O}_3 \), the oxygen exchange increasing in this order. The presence of methane did not influence the exchange rate.

The reactivity of adsorbed versus lattice oxygen is also a point of interest. Buyevskaya et al. (1994A) reported that surface lattice oxygen of pure MgO is responsible for methyl radical formation resulting in \( \text{C}_2 \) products, while adsorbed oxygen species take part in the total oxidation reactions. Two different active sites for the formation of \( \text{C}_2 \) products and carbon oxides were reported on \( \text{Sm}_2\text{O}_3 \), Li/\( \text{Sm}_2\text{O}_3 \) and Pr\(_6\)O\(_{11}\) (Ekstrom and Lapszewicz, 1989), Li/MgO (Peil et al., 1989; Peil et al., 1991) and PbO/MgO (Asami et al., 1987), whereas parallel paths for selective and non-selective reactions are also reported by other authors for Li/MgO (Nibbelke et al., 1995; Nelson et al., 1989; Mirodatos et al., 1990; Couwenberg, 1995). However, in the case of Pr\(_6\)O\(_{11}\) lattice oxygen catalyses the direct conversion of methane to carbon dioxide (Ekstrom and Lapszewicz, 1989). The activity of Li/NiO was mainly related to lattice oxygen, which catalyses the selective reactions, while adsorbed oxygen promotes full oxidation (Sun et al., 1993). The lattice oxygen may be considered as a Li-Ni oxide phase. For Li/TiO\(_2\) a large pool of oxygen species participating in the formation of carbon dioxide was reported, while subsurface lattice oxygen species also participate in the oxygen reaction pathway to form carbon dioxide (Efstathiou et al., 1994).

The objective of the study presented in this chapter was to investigate the interaction of oxygen with MgO, Li/MgO and Sn/Li/MgO. The reactivity of both adsorbed and surface lattice oxygen was studied as well. A mechanism for the
reaction pathways of oxygen during the oxidative coupling of methane over MgO based catalysts is postulated.

5.2 Experimental procedures and definitions

The number of molecules admitted per single TAP pulse was in the range of $10^{16} - 10^{17}$, resulting in an average total pressure of 1000 Pa above the catalyst surface during 100 ms. In a single pulse the ratio of admitted methane as well as oxygen molecules to the theoretical number of surface oxygen atoms was always below 0.03. The catalysts used in this investigation were magnesium oxide, lithium on magnesium oxide (Li/MgO) and tin promoted lithium on magnesium oxide (Sn/Li/MgO); their characterisation is described in section 2.5.1.1. Non-porous $\alpha$-Al$_2$O$_3$ with a grain size of 0.21 to 0.25 mm was used as inert packing material.

The inconel microreactor was charged with 0.1 to 0.4 g of catalyst and packed with inert material at each end. Two thermocouples were inserted into the catalyst bed for temperature measurements. Blank pulse experiments of methane as well as methane with oxygen over $\alpha$-Al$_2$O$_3$ showed a conversion of two percent, which is negligible compared to conversions obtained in the presence of a catalyst. In all experiments argon was added to the admitted gases as a reference component for calculation of the conversion of the reactants and the amount of admitted molecules.

The catalyst was pretreated according to the procedure mentioned in section 2.5.1.2. Furthermore, prior to each experiment the catalyst was exposed to a steady flow of oxygen during five minutes after which adsorbed oxygen was removed by maintaining a vacuum of $10^{-5}$ Pa during five minutes.

The experiments were carried out in the temperature range of 923 K to 1073 K. Only ethane and carbon monoxide were observed during the interaction of methane or methane and oxygen with the surface. No formation of ethene was observed. In the case of Li/MgO and Sn/Li/MgO it was not possible to detect carbon dioxide quantitatively at the reactor outlet due to its strong adsorption on the catalyst surface. Pulse experiments with carbon dioxide showed no breakthrough up to a temperature of 973 K. Therefore carbon dioxide formation was deduced from the carbon balance, although methyl radicals could not be accounted for quantitatively. Only in the case of MgO carbon dioxide can be detected quantitatively. In the case of pulse experiments with labelled oxygen the mass balance was closed within seven percent.
For each experiment the conversion and yields were calculated according to the following equations:

\[ X_{CH_4} = \frac{n_{in,CH_4} - n_{out,CH_4}}{n_{in,CH_4}} \]  
(5.1)

\[ Y_{C_2H_6} = \frac{2n_{out,C_2H_6}}{n_{in,CH_4}} \]  
(5.2)

\[ Y_{CO} = \frac{n_{out,CO}}{n_{in,CH_4}} \]  
(5.3)

\[ Y_{CO_2} = \frac{n_{in,CH_4} - n_{out,CH_4} - n_{out,CO} - 2n_{out,C_2H_6}}{n_{in,CH_4}} \]  
(5.4)

\[ X_{18O_2} = \frac{n_{in,18O_2} - n_{out,18O_2}}{n_{in,18O_2}} \]  
(5.5)

\[ Y_{16O18O} = \frac{n_{out,16O18O}}{n_{in,18O_2}} \]  
(5.6)

\[ Y_{16O_2} = \frac{n_{out,16O_2}}{n_{in,18O_2}} \]  
(5.7)

where \( n \) is the total number of moles (mol), \( X \) is the conversion (mol mol\(^{-1}\)) and \( Y \) is the yield (mol mol\(^{-1}\)). The subscript "in" means introduced into the reactor and the subscript "out" means detected at the reactor outlet.

Activation energies were derived from the observed linear dependence of \( \ln X \) on the inverse temperature, applying an identical amount of molecules per pulse at various temperatures. Only measurements with a conversion lower than 50 % were selected for determination of the activation energies.
5.3 Results

5.3.1 Interaction of oxygen with the surface

The interaction of oxygen with the catalytic surfaces was investigated with multipulse experiments of oxygen, with a four seconds time interval between the pulses. The exchange between gaseous oxygen and surface lattice oxygen was studied on MgO and Sn/Li/MgO with pulse experiments of labelled oxygen, $^{18}$O$_2$.

Sn/Li/MgO

The responses of a multipulse experiment at 973 K are shown in Figure 5.1. The surface area of the individual oxygen responses increases for the first pulses to remain subsequently constant. The initial lower oxygen signals are attributed to oxygen interacting strongly with the catalyst surface. This strongly adsorbed oxygen desorbs completely on a time scale of three minutes at 973 K.

![Figure 5.1: Response of oxygen as a function of time at 923 K. Multipulse experiment of oxygen over 0.11 g of Sn/Li/MgO with a pulse intensity of 5 $10^{16}$ molecules.](image)

All individual responses of oxygen are broadened when compared to argon, as shown in Figure 5.2, which points to a second type of oxygen species interacting with the catalyst surface. This type is referred to as weakly adsorbed oxygen and the time interval required for complete desorption amounts to four seconds at 973 K.
A reaction path analysis of the catalytic partial oxidation of methane by transient experiments

Figure 5.2: Normalised responses of oxygen and argon as a function of time at 973 K. Pulse experiment of oxygen and argon over 0.11 g of Sn/Li/MgO with a pulse intensity of $5 \times 10^{16}$ molecules. Ten pulses were introduced prior to the experiment.

The amount of strongly adsorbed oxygen, expressed as a percentage of the theoretical number of surface oxygen atoms, is presented in Table 5.1, based on $1.26 \times 10^{19}$ oxygen atoms per square meter. The amount increases with increasing temperature. The activation energy for the interaction of oxygen via the strongly adsorbed oxygen species amounts to 35 kJ mol$^{-1}$, as derived from the first pulse of the multipulse experiment.

Table 5.1: Amount of strongly adsorbed oxygen, expressed as a percentage of a theoretical monolayer, present on 0.35 g of Li/MgO and 0.11 g of Sn/Li/MgO at various temperatures ranging from 923 K to 1023 K, as obtained from multipulse experiments of oxygen with a pulse intensity of $5 \times 10^{16}$ molecules.

<table>
<thead>
<tr>
<th>T / K</th>
<th>Li/MgO / %</th>
<th>Sn/Li/MgO / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>923</td>
<td>5.1</td>
<td>4.7</td>
</tr>
<tr>
<td>948</td>
<td>6.3</td>
<td>6.3</td>
</tr>
<tr>
<td>973</td>
<td>8.1</td>
<td>6.9</td>
</tr>
<tr>
<td>998</td>
<td>10.2</td>
<td>9.1</td>
</tr>
<tr>
<td>1023</td>
<td>11.5</td>
<td>10.6</td>
</tr>
</tbody>
</table>

The interaction of oxygen with the surface via the weakly adsorbed species was further investigated by pulse experiments of labelled oxygen. Prior to each
experiment ten single pulses of labelled oxygen were introduced in order to reach the maximum concentration of strongly adsorbed oxygen, necessary for closed oxygen balances.

During the interaction of labelled oxygen with the surface the exchange products $^{16}\text{O}^{18}\text{O}$ as well as $^{16}\text{O}_2$ were produced. The normalised responses of $^{18}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$ and $^{16}\text{O}_2$ at a temperature of 773 K are shown in Figure 5.3. The response of $^{18}\text{O}_2$ is observed first, followed by that of $^{16}\text{O}^{18}\text{O}$ and finally $^{16}\text{O}_2$.

The conversion of $^{16}\text{O}_2$ increases from 40 % at 773 K to 90 % at 923 K. The yield of $^{16}\text{O}^{18}\text{O}$ shows a maximum of 50 %, while that of $^{16}\text{O}_2$ increases from 10 % to 42 %. The activation energy for the interaction of oxygen via the weakly adsorbed species amounts to 35 kJ mol$^{-1}$.

![Figure 5.3: Normalised responses of $^{18}\text{O}_2$, $^{16}\text{O}^{18}\text{O}$ and $^{16}\text{O}_2$ as a function of time at a temperature of 773 K. Pulse experiment of labelled oxygen over 0.10 g Sn/Li/MgO with a pulse intensity of 5 $10^{16}$ molecules. Ten pulses of labelled oxygen were introduced prior to the experiment.](image)

Li/MgO

The results of a multipulse experiment are qualitatively identical to those obtained on Sn/Li/MgO. The surface area of the oxygen responses increases for the first pulses to remain subsequently constant, pointing to a first type of oxygen species interacting strongly with the surface. It desorbs completely on a time scale of three minutes at 973 K.

The amount of strongly adsorbed oxygen is also presented in Table 5.1 and similar to that of Sn/Li/MgO when expressed per unit BET surface area. However, the activation energy for the interaction of oxygen with the surface via strongly adsorbed oxygen amounts to 92 kJ mol$^{-1}$, which is significantly higher compared
to the value obtained for Sn/Li/MgO.

All responses are broadened with respect to argon, pointing to weakly adsorbed oxygen species on the surface, which desorb on a time scale of three seconds at 973 K.

MgO

An immediate and complete breakthrough of oxygen was observed in a multipulse experiment with oxygen, which means that oxygen species showing a strong interaction with the surface are not present. Weakly adsorbed oxygen species are present, as concluded from the peak broadening compared to argon, which was further investigated with labelled oxygen experiments. Again, the response of $^{18}\text{O}_2$ is observed first, followed by that of $^{16}\text{O}^{18}\text{O}$ and $^{16}\text{O}_2$. The conversion of labelled oxygen increases from 10 % at 773 K to 77 % at 923 K. The corresponding yields to $^{16}\text{O}^{18}\text{O}$ and $^{16}\text{O}_2$ increase from 8 and 2 % to 53 % and 24 %.

Weakly adsorbed oxygen desorbs on a time scale of 0.5 s at 923 K and the activation energy for the interaction of oxygen with the surface amounts to 120 kJ mol\(^{-1}\).

5.3.2. Reactivity of adsorbed oxygen species

The reactivity of adsorbed oxygen species was investigated with alternating pulse experiments pulsing first oxygen and next either methane, ethane, ethene or carbon monoxide, at a methane to oxygen feed molar ratio of 2 to 3 in order to ensure a complete reoxidation of the catalyst. In the case of Sn/Li/MgO no oxygen breakthrough was observed.

Sn/Li/MgO

Seven different time intervals were applied between the oxygen and methane pulses, varying from zero, i.e. simultaneous pulsing, up to 10 s. The experiments were carried out at a temperature of 973 K. The conversion of methane decreases from 60 % to 44 % with increasing time interval due to the disappearance of weakly adsorbed oxygen species, having a time scale for desorption of four seconds at 973 K. However, the yield of ethane and carbon monoxide remain constant at varying time interval at 0.45 % and 0.11 %, meaning that weakly adsorbed oxygen only contributes to methane conversion into carbon dioxide.

Six different time intervals were applied between the oxygen and ethane pulse, varying from zero up to 5 s at a temperature of 973 K. The corresponding
conversion of ethane decreases from 69 % to 57 %, the latter being equal to that obtained during the interaction of ethane with surface lattice oxygen alone. The yield of carbon monoxide and carbon dioxide decreases accordingly. The produced amount of ethene was already low in the case of simultaneous pulsing and vanishes completely at the smallest time interval which was applied, \( i.e. \) 20 ms.

In the case of ethene and carbon monoxide alternating pulse experiments were carried out at 973 K and 773 K. The conversions decrease from 57 % and 98 % at a time interval of 0 s to 51 % and 93 % at a time interval of 4 s. For ethene the yields of carbon monoxide and carbon dioxide decrease accordingly. The final conversion levels are identical to those obtained during the interaction of ethene and carbon monoxide with surface lattice oxygen alone.

**MgO**

At a temperature of 1050 K six different time intervals were applied between the oxygen and methane pulse, varying from simultaneous pulsing up to 0.09 s. Since strongly adsorbed oxygen species are not present in the case of MgO a closed oxygen balance can be obtained during a single pulse of oxygen.

![Figure 5.4](image)

**Figure 5.4:** Responses of oxygen as a function of time at a temperature of 1050 K for 0.13 g of MgO with a pulse intensity of \( 9 \times 10^{16} \) molecules of oxygen. Line A: pulse experiment of oxygen. Line B: alternating pulse experiment of oxygen followed by methane at a time interval of 0.06 s. Methane to oxygen feed molar ratio of 0.5

A typical response of oxygen is presented in Figure 5.4 together with a response resulting from pulsing oxygen alone. As soon as methane is introduced into the reactor, the response of oxygen abruptly decreases. This behaviour is attri-
buted to the conversion of weakly adsorbed oxygen species by methane, which are created by dioxygen as shown in the previous section.

The amount of weakly adsorbed oxygen being titrated by methane is calculated from the difference in the surface area of both responses for all the different time intervals applied, as proposed by Buyevskaya et al. (1994B). The second maximum in the oxygen response is attributed to a pressure wave due to the introduction of methane and argon, rather than to desorption of weakly molecularly adsorbed species, as proposed by Buyevskaya et al. (1994B).

In Figure 5.5 the conversion of methane versus the amount of weakly adsorbed oxygen, expressed as a percentage of a theoretical monolayer, is presented. The conversion of methane amounts to 4% in the presence of surface lattice oxygen alone.

![Graph](image_url)

**Figure 5.5:** Conversion of methane versus the amount of adsorbed oxygen, expressed as a percentage of a theoretical monolayer, for 0.13 g of MgO at a temperature of 1050 K. Methane to oxygen feed molar ratio of 0.5 and a pulse intensity of $5 \times 10^{16}$ molecules for methane. Filled square denotes to the methane conversion obtained in the presence of surface lattice oxygen alone.

The yield of ethane, carbon monoxide and carbon dioxide versus the amount of weakly adsorbed oxygen are presented in Figure 5.6, together with the values obtained in the presence of surface lattice oxygen alone. The yield of ethane and carbon monoxide is almost constant, while that of carbon dioxide increases with increasing amount of weakly adsorbed oxygen.
**Figure 5.6:** Yield of ethane, carbon monoxide and carbon dioxide versus the amount of adsorbed oxygen, expressed as a percentage of a theoretical monolayer, for 0.13 g of MgO at a temperature of 1050 K. Methane to oxygen feed molar ratio of 0.5 and a pulse intensity of $5 \times 10^{16}$ molecules for methane. Filled symbols denote the yields obtained in the presence of surface lattice oxygen alone.

### 5.3.3. Reactivity of surface lattice oxygen

The reactivity of surface lattice oxygen was investigated by multipulse experiments of methane alone with a 0.4 s time interval between the pulses. A time interval of five minutes between the oxygen treatment and the start of the experiment was applied, during which both strongly and weakly adsorbed oxygen species were removed from the surface.

**Sn/Li/MgO**

The surface area of the methane responses increases for the first pulses to remain subsequently constant. Figure 5.7 presents the conversion of methane and yield of ethane as a function of the pulse number. At the first pulse of methane the conversion amounts to 43 %, while the yield of ethane amounts to 0.46 % and that of carbon monoxide to 0.12 %. These values are identical to those obtained in the alternating pulse experiment applying a time interval of ten seconds between the oxygen and methane pulse. The decrease of the methane conversion is much more pronounced compared to that of the yield of ethane.
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Figure 5.7: Conversion of methane and yield of ethane as a function of the pulse number. Multipulse experiment of methane over 0.42 g of Sn/Li/MgO at a temperature of 973 K and a pulse intensity of $7 \times 10^{16}$ molecules.

The total amount of reactive surface lattice oxygen was determined from the amount of converted methane with the assumption that carbon dioxide and water are the only reaction products, i.e. corresponding to the consumption of four oxygen atoms per converted methane molecule. The assumption is valid, since the combined yield to ethane and carbon monoxide is less than one percent.

Table 5.2: Amount of reactive surface lattice oxygen, expressed as a percentage of a theoretical monolayer, for 0.40 g of Li/MgO and 0.42 g of Sn/Li/MgO at various temperatures, as obtained from multipulse experiments of methane with a pulse intensity of $7 \times 10^{16}$ molecules.

<table>
<thead>
<tr>
<th>T / K</th>
<th>Li/MgO / %</th>
<th>Sn/Li/MgO / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>923</td>
<td>0.9</td>
<td>6.7</td>
</tr>
<tr>
<td>948</td>
<td>1.6</td>
<td>11.3</td>
</tr>
<tr>
<td>973</td>
<td>2.8</td>
<td>16.7</td>
</tr>
<tr>
<td>998</td>
<td>7.7</td>
<td>29.2</td>
</tr>
<tr>
<td>1023</td>
<td>27.2</td>
<td>43.9</td>
</tr>
<tr>
<td>1048</td>
<td>41.6</td>
<td>-</td>
</tr>
</tbody>
</table>

The amount of reactive surface lattice oxygen is presented in Table 5.2, ex-
pressed as a percentage of a theoretical monolayer, and amounts to 44% at 1023 K. The activation energy for methane conversion amounts to 86 kJ mol⁻¹ as derived from the first pulse of the multipulse experiment.

**Li/MgO**

The surface area of the individual responses increases and finally remains constant. The amount of reactive surface lattice oxygen is presented in Table 5.2. As in the case of Sn/Li/MgO, the amount increases at increasing temperature and corresponds to 42% of a theoretical monolayer at 1048 K. However, the percentage of reactive surface lattice oxygen is always low compared to that of Sn/Li/MgO at the same temperature. The activation energy for methane conversion amounts to 85 kJ mol⁻¹ as derived from the first pulse of the multipulse experiment.

**MgO**

The surface area of the individual methane responses is constant, except for the first pulse. The amount of reactive surface lattice oxygen is less than 0.1% of a theoretical monolayer at temperatures between 873 and 1073 K. During the first pulse at 1048 K the conversion of methane amounts to 4%, while the yield to ethane amounts to 0.59% and that to carbon monoxide to 2.2%.

5.4 Discussion

5.4.1 Reaction network

Based on previous work (Mallens et al., 1994) a reaction network for the oxidative coupling of methane over Sn/Li/MgO in the presence of both methane and oxygen at 973 K was proposed, which is shown in Figure 5.8. Methyl radicals are produced at the catalyst surface and combine in the gas phase to form ethane (Ito et al., 1985; Nelson et al., 1988). Ethene is produced from ethane via a gas phase reaction in which dioxygen is involved. It is assumed that this reaction occurs via surface generated ethyl radicals, as shown for Li/MgO (Morales and Lunsford, 1989). Both ethane and ethene are oxidised to carbon monoxide at the surface. Carbon monoxide is oxidised to carbon dioxide by interaction with the surface (Peil et al., 1989; van der Wiele et al., 1992). In parallel to the formation of ethane, methane is directly converted to carbon dioxide.

The present study allows to specify the role of both adsorbed and surface lattice oxygen in the oxidative coupling of methane.
A reaction path analysis of the catalytic partial oxidation of methane by transient experiments

\[
\begin{align*}
\text{CH}_4 & \rightarrow \text{CH}_3 \rightarrow \text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 \\
\text{O}_{\text{ads}} & \rightarrow \text{O}_L^I \rightarrow \text{CO} \rightarrow \text{CO}_2
\end{align*}
\]

**Figure 5.8:** Reaction network and role of different oxygen species in the oxidative coupling of methane in the presence of oxygen over Sn/Li/MgO at 973 K. \(\text{O}_{\text{ads}}\) = weakly adsorbed oxygen species, \(O_L^I\) = first type of reactive surface lattice oxygen and \(O_L^{II}\) = second type of reactive surface lattice oxygen.

5.4.2 Interaction of oxygen with the surface

The results of the multipulse experiments, see Figure 5.1, indicate that in the case of Li/MgO and Sn/Li/MgO both strongly and weakly adsorbed oxygen species are present on the surface. However, for MgO only weakly adsorbed oxygen exists. This result is in line with those of Nakamura et al. (1993), who studied the formation of adsorbed oxygen species by the decomposition of \(\text{N}_2\text{O}\) on MgO and Li/MgO. The temperature programmed desorption of the oxygen species revealed that two types of adsorbed species were present on Li/MgO, referred to as \(\alpha\)- and \(\beta\)-oxygen species. A weak \(\alpha\)-oxygen peak occurred on MgO and no \(\beta\)-oxygen peak was observed.

For the present study, the formation of weakly adsorbed oxygen species on the promoted catalysts is attributed to the interaction of dioxygen with the MgO phase. The presence of the strongly adsorbed oxygen species is related to a lithium phase. Peng et al. (1990) reported two forms of lithium, i.e. \(\text{Li}^+\text{O}^-\) centers and \(\text{Li}_2\text{CO}_3\), on the surface of Li/MgO under reaction conditions. For the Li/MgO and Sn/Li/MgO catalysts two crystalline phases were detected by XRD measurements: MgO and \(\text{Li}_2\text{CO}_3\) (Couwenberg, 1995).

During the pretreatment of the promoted catalysts large amounts of carbon dioxide were detected quantitatively. This is assigned to the decomposition of the \(\text{Li}_2\text{CO}_3\) phase into a \(\text{Li}_2\text{O}\) phase, which leads to the conclusion that \(\text{Li}_2\text{O}\) is present as well at the experimental conditions of the present study. However, it is not clear
whether both phases are simultaneously present. The presence of either a Li_2O or a Li_2CO_3 phase is considered to be responsible for the formation of strongly adsorbed oxygen in the case of the promoted catalysts.

The amount of strongly adsorbed oxygen increases with increasing temperature, as shown in Table 5.1, and is essentially identical for Li/MgO and Sn/Li/MgO. Peng et al. (1990) reported that in the case of Li/MgO at lithium loadings of 1 to 10 wt. % the concentration of Li^+O and Li_2CO_3 at the surface did not change. Assuming this is also the case for Sn/Li/MgO this observation explains the identical amounts of strongly adsorbed oxygen reported for both promoted catalysts, though the percentage of lithium is different for Li/MgO and Sn/Li/MgO, see Table 2.3.

The interaction of oxygen with the surface via weakly adsorbed oxygen species was investigated by pulse experiments with labelled oxygen. Nibbelke et al. (1995) observed that both surface and lattice oxygen participate in the oxygen exchange reaction for Li/MgO and Sn/Li/MgO. It can be assumed that for all catalysts in the present study solely the interaction of labelled dioxygen with surface lattice oxygen was studied. Indeed, the average residence time of oxygen in the catalyst bed amounts to 0.1 seconds, whereas the characteristic time for diffusion of oxygen through one layer of the bulk lattice amounts to 190 seconds in the case of MgO and to 1 second in the case of Sn/Li/MgO, based on values of the diffusion coefficients estimated by Nibbelke et al. (1995) and a distance between two layers of 1.98 \times 10^{-10} m. Hence, the characteristic time for diffusion of oxygen into one monolayer of the bulk is one to three orders of magnitude larger than the average residence time in the reactor.

The results indicate that the adsorption of oxygen is reversible and dissociative both on MgO and Sn/Li/MgO, since formation of \(^{16}\text{O}^{18}\text{O}\) was observed. The normalised response of \(^{16}\text{O}^{18}\text{O}\) is observed prior to that of \(^{16}\text{O}_2\), see Figure 5.3, which points to the primary formation of \(^{16}\text{O}^{18}\text{O}\) followed by \(^{16}\text{O}_2\). This result is in line with a mechanism proposed by Winter (1968, 1969), who studied the kinetics of oxygen exchange between labelled oxygen and several metal oxides, including MgO:

\[
^{18}\text{O}_2 + ^{16}\text{O}_{\text{lattice}} \rightleftharpoons ^{16}\text{O}^{18}\text{O} + ^{18}\text{O}_{\text{lattice}}
\]

\[
^{16}\text{O}^{18}\text{O} + ^{16}\text{O}_{\text{lattice}} \rightleftharpoons ^{16}\text{O}_2 + ^{18}\text{O}_{\text{lattice}}
\]

i.e. involving the participation of a single atom of lattice oxygen in the oxygen exchange reaction.

The conversion of labelled dioxygen into exchange products increases at increasing temperature with an increasing yield to the consecutive exchange product \(^{16}\text{O}_2\). For Sn/Li/MgO a maximum in the yield to \(^{16}\text{O}^{18}\text{O}\) was observed in the investigated temperature range. The activation energy for oxygen exchange on
MgO amounts to 120 kJ mol\(^{-1}\), which is in the same order of magnitude as the value of 159 kJ mol\(^{-1}\) reported by Winter (1968) for MgO.

Winter postulated that the exchange reaction was confined to the surface layer, as is the case in the present study. However, the activation energy of 120 kJ mol\(^{-1}\) is much lower than the value of 261 kJ mol\(^{-1}\) reported by Buyevskaya et al. (1994B) for the oxygen exchange on MgO. The authors compare their value to the activation energy of 266 kJ mol\(^{-1}\) for oxygen diffusion in the bulk of MgO (Peil et al., 1991) and argue that oxygen diffusion might be the rate limiting step under the applied conditions. In the case of Sn/Li/MgO the activation energy for oxygen exchange is much lower compared to MgO, amounting to 35 kJ mol\(^{-1}\). The large decrease in the activation energy leads to a large increase in the concentration of oxygen on the catalyst available for exchange with gas phase oxygen due to the promotion with lithium and tin (Nibbelke et al., 1995). For MgO the concentration of oxygen on the catalyst only amounts to 10 % of a theoretical monolayer, while for the lithium promoted catalysts, especially for Sn/Li/MgO, the value of a theoretical monolayer is exceeded. This phenomenon is attributed to subsurface oxygen immediately available for exchange by Peil et al. (1991). A different explanation is that in the case of the lithium promoted catalysts the exchange of oxygen occurs via the lithium oxide phase.

5.4.3 Reactivity of adsorbed oxygen species

The weakly adsorbed oxygen species are very reactive towards methane compared to surface lattice oxygen, as shown in Figure 5.5. A linear dependence of the methane conversion on the amount of weakly adsorbed oxygen species is observed for MgO. The extrapolated conversion of methane in the absence of adsorbed oxygen species agrees well with the experimentally observed value of 4 % in the presence of surface lattice oxygen alone.

In the case of Sn/Li/MgO the conversion of methane decreases due to the disappearance of adsorbed species and reaches a constant value after a time interval of four seconds between the oxygen and methane pulse. The final conversion level is identical to the value obtained during the interaction of methane with surface lattice oxygen alone.

The strongly adsorbed oxygen species are still present after a time interval of four seconds up to three minutes, which leads to the conclusion that these species are not active in the methane conversion at all.

For both catalysts the yields of ethane and carbon monoxide do not depend on the concentration of weakly adsorbed oxygen species and are identical to the yields obtained during the interaction of methane with surface lattice oxygen alone, as shown in Figure 5.6 for MgO. This leads to the conclusion that in the presence
of weakly adsorbed oxygen, denoted $O_{\text{ads}}$ in Figure 5.8, methane is directly converted to carbon dioxide. This reaction occurs in parallel to the activation of methane via surface lattice oxygen. A direct reaction path from methane to carbon dioxide was also concluded when pulsing methane and oxygen simultaneously over MgO (Mallens et al., 1994).

In the case of ethane, ethene and carbon monoxide both surface lattice oxygen and weakly adsorbed oxygen species are involved in the non-selective reaction paths. At increasing time interval between the oxygen and reductant pulse the conversion and yields to the products decrease and finally a constant level is reached, identical to the values obtained in the presence of surface lattice oxygen alone. Strongly adsorbed oxygen species are not reactive towards these reductants at all.

The reactivity of Sn/Li/MgO towards ethane is higher compared to ethene, which is in line with the difference in the dissociation energy of the C-H bond in ethane of 418 kJ mol$^{-1}$ and ethene of 443 kJ mol$^{-1}$ (Weast, 1987) and with the observation that ethene shows no significant interaction with the catalyst (Nibbelke et al., 1995). At first sight, ethene is expected to exhibit a stronger interaction with the catalyst than methane because of the double bond in ethene. The high basicity of Sn/Li/MgO probably prevents the interaction of ethene with the catalyst.

5.4.4 Reactivity of surface lattice oxygen

The amount of surface lattice oxygen which is reactive towards methane is less than 0.1 % of a theoretical monolayer in the case of MgO up to temperatures of 1073 K. For Li/MgO and Sn/Li/MgO the percentage of reactive surface lattice oxygen is one to two orders of magnitude higher and the amount increases at increasing temperature. The Sn/Li/MgO catalyst possesses the highest amount at a comparable temperature, see Table 5.2.

In the investigated temperature range the amount of reactive surface lattice oxygen is always less than one theoretical monolayer of atomic oxygen. Sinev et al. (1989) reported the removal of an amount of oxygen equivalent to 40 % of a theoretical monolayer by exposure of Li/MgO to hydrogen at 823 K, which is in the same order of magnitude as reported in the present study.

The addition of a reducible oxide, such as SnO$_2$, to Li/MgO further increases the activity of the catalyst (Korf et al., 1989; Larkins and Nordin, 1988; Yingli et al., 1988; Bartsch et al., 1989). The oxidation state of Sn in the Sn/Li/MgO catalyst was investigated by means of Mössbauer spectrometry. The results showed that the bulk Sn phase consisted only of SnO$_2$ when the catalyst was pretreated with pure oxygen or a methane and oxygen mixture at 1023 K. In the latter case a methane to oxygen molar ratio of 10 was applied and complete
conversion of oxygen was achieved. However, thirty atom percent was in the form of metallic Sn after pretreatment with pure methane at 1023 K. No SnO was detected quantitatively after any of the above pretreatments.

The decrease of the methane conversion and the yield of ethane with increasing pulse number is different on both Sn/Li/MgO and Li/MgO, see Figure 5.7. This points to two different types of surface lattice oxygen, one type being involved in the selective conversion of methane to ethane, denoted $O_L^I$ in Figure 5.8. A second type, $O_L^{II}$, is reactive in the non-selective conversion of methane to carbon dioxide, as concluded from the fast decrease in the methane conversion.

5.4.5 Comparison between MgO, Li/MgO and Sn/Li/MgO

The identical activation energy for the interaction of oxygen via weakly and strongly adsorbed oxygen with Sn/Li/MgO points to a common rate determining step for the formation of both types of species. A possible mechanism is the formation of weakly adsorbed species via oxygen vacancies in the MgO phase, after which species adsorbed in the neighbourhood of a $Li_2O$ or a $Li_2CO_3$ phase are transferred to this phase via spill-over. The amount of the oxygen vacancies in the MgO lattice increases due to the addition of lithium to MgO (Lacey et al., 1978).

The activation energy for the formation of both weakly and strongly adsorbed oxygen species decreases in the order of MgO, Li/MgO and Sn/Li/MgO. Dioxygen must be converted to the form of $O^-$ or $O^{2-}$ at the surface before it reacts and apparently the addition of lithium and moreover tin facilitates this process.

The activation energy for methane conversion over surface lattice oxygen amounts for Li/MgO and Sn/Li/MgO to 85 kJ mol$^{-1}$ and 86 kJ mol$^{-1}$, which indicates that the reaction proceeds on both catalysts via a common rate determining step. These values are in reasonable agreement with literature results. A value of 54 kJ mol$^{-1}$ was reported for the interaction of methane with Li/MgO in the absence of dioxygen (Bychkov et al., 1989), while values of 87 kJ mol$^{-1}$ for Li/MgO (Amorebieta and Colussi, 1988) and 123 kJ mol$^{-1}$ for Sn/Li/MgO (Couwenberg, 1995) were reported for the methane interaction step with the surface.

An increase in the activity of Li/MgO by the addition of SnO$_2$ was reported by Korf et al. (1989), as concluded from the lower reaction temperature necessary in the case of Sn/Li/MgO for identical oxygen conversion and yields to $C_2$ products. The value of the activation energy for the catalytic activation step of methane is identical for both catalysts, as mentioned in the previous section. The value of the preexponential factor for this reaction step is also identical for both Li/MgO and Sn/Li/MgO, as reported by Couwenberg (1995). Therefore, the increase in the activity of Sn/Li/MgO compared to Li/MgO is attributed to the observed increase
in the amount of reactive surface lattice oxygen. The latter results from an increase in the lattice oxygen mobility, as indicated by an increasing oxygen diffusion coefficient in the bulk of the lattice (Nibbelke et al., 1995). Indeed, at 1000 K the ratio of the amount of reactive surface lattice oxygen of Sn/Li/MgO compared to Li/MgO amounts to 1.6. This ratio compares quite well with the rate of the heterogeneous methane activation for both catalysts, expressed per unit BET surface area, of 2.4 at 1023 K, 110 kPa and an initial methane to oxygen molar ratio of 4, which follows from values for the reaction rate coefficients estimated by Couwenberg (1995).

5.4.6 Reaction mechanism

In spite of the low yields of C₂ products, the results of the present study are relevant for the heterogeneous reaction steps in the oxidative coupling of methane, where a typical yield of 20 % is obtained with Sn/Li/MgO (Couwenberg, 1995).

The interaction of methane and oxygen with the catalyst has been investigated at an average pressure of 1000 Pa, which is low compared to industrially relevant pressures which are in the range of 100 to 1000 kPa. The coupling of two methyl radicals to ethane has to occur in the gas phase but is at 1000 Pa in the low pressure regime according to the unimolecular rate theory of Rice-Ramsperger-Kassel-Marcus (Robinson and Holbrook, 1972) and pressure fall-off data from the literature (Chen et al., 1994A). Ethene is not detected at 1000 Pa since the formation also has to occur in the gas phase by involvement of dioxygen. The direct decomposition of ethyl radicals towards ethene can be ruled out at pressures of 1000 Pa (Chen et al., 1994A). Hence, as a result of the low pressures the yield of C₂ products is less than one percent in the present study and the experimental data obtained with methane pulses will provide information on the generation of methyl radicals rather than on the global coupling reaction.

The role of different oxygen forms in the oxidative coupling of methane over Sn/Li/MgO in the presence of both methane and oxygen can be specified and is shown in Figure 5.8, together with the proposed network. The formation of methyl radicals from methane proceeds via one form of surface lattice oxygen, denoted O_L in Figure 5.8. It seems likely that these sites are also involved in the formation of ethyl radicals from ethane. Both weakly adsorbed oxygen species, O_ads, and a second form of surface lattice oxygen, O_L II, are involved in the non-selective reaction path of methane to carbon dioxide. The oxidation of ethane and ethene to carbon monoxide and the consecutive oxidation of carbon monoxide also proceed via weakly adsorbed oxygen species, O_ads. Surface lattice oxygen is involved as well and it seems likely that only the non-selective form, O_L II, contributes to these reactions. Strongly adsorbed oxygen species are not involved
in the reaction mechanism of the oxidative coupling of methane.

Peil et al. (1991) propose two parallel carbon pathways for the conversion of methane over Li/MgO, one for the formation of $C_2H_6$ and the second for $CO_x$ formation. The sites for the carbon reaction pathway involved in the formation of $C_2H_6$ have a lower activity than sites involved in the formation of CO and $CO_2$. Also, CO and $CO_2$ may be formed sequentially on the surface, with lattice oxygen participating in the reaction. Parallel formation of $C_2H_6$ and $CO_x$ over Li/MgO has also been reported by Mirodatos et al. (1990) and Nelson et al. (1989). A possible mechanism is that methyl radicals either desorb and couple in the gas phase to form $C_2H_6$ or react with surface oxygen to produce $CO_x$.

The direct formation of $CO_2$ from methane over Sn/Li/MgO is in line with the work of Nibbelke et al. (1995) and Couwenberg (1995). Under reaction conditions a strong interaction of both the oxygen and carbon atoms leading to carbon dioxide was observed due to the surface catalysed formation of $CO_2$ as well as the interaction of $CO_2$ with the catalyst. The latter is believed to be the result from transformation of lithium oxide, Li$_2$O, into lithium carbonate, Li$_2$CO$_3$, by $CO_2$. A methoxy species was postulated as the intermediate in the reaction path to $CO_2$, based on modelling results. Bytyn and Baerns (1986) also proposed formation of a methoxy species in the non-selective pathways of the oxidative coupling of methane over supported PbO catalysts. The network proposed in Figure 5.8 is consistent with the following mechanism for the production of methyl radicals, in line with that originally proposed by Lunsford and coworkers (Ito et al., 1985):

$$O_2 + 2 \cdot \rightarrow 2 O \cdot \quad (5.9)$$

$$CH_4 + O \cdot \rightarrow OH \cdot + CH_3 \cdot \quad (5.10)$$

$$OH \cdot + OH \cdot \rightarrow H_2O + O \cdot + \cdot \quad (5.11)$$

The reversible chemisorption of dioxygen followed by transformation leading to the four different forms of oxygen species is summarised by reaction 5.9. Only one of these forms, denoted $O_L^1$ in Figure 5.8, is involved in the H abstraction from methane according to an Eley-Rideal mechanism, as described by reaction 5.10. It was shown by Chen et al. (1994B) that the rate of regeneration of the active sites, reaction 5.11, is kinetically significant on Sn/Li/MgO. The rate of transformation leading to $O_L^1$ and possibly that of regeneration of active sites may be increased by an increasing lattice oxygen mobility.
5.5 Conclusions

Two types of oxygen species are present on the surface of Sn/Li/MgO. The first type is strongly adsorbed oxygen interacting with a Li$_2$O or Li$_2$CO$_3$ phase. This type of oxygen does not seem active in methane coupling. The second type of oxygen concerns weakly adsorbed oxygen species, which are involved in the direct conversion of methane to carbon dioxide.

The percentage of surface lattice oxygen active in the methane conversion is less than 0.1 % for MgO but increases for Li/MgO and even more for Sn/Li/MgO. On Sn/Li/MgO two types of surface lattice oxygen are present. The first type activates methane for the methyl radical formation, while the second is involved in the direct conversion of methane to carbon dioxide.

Both weakly adsorbed oxygen species and the second type of surface lattice oxygen are involved in the non-selective reaction paths of ethane and ethene as well as the consecutive oxidation of carbon monoxide.

The observations are consistent with the Lunsford mechanism for the generation of methyl radicals over MgO based catalysts. The increasing activity towards methane due to the addition of lithium and moreover tin to MgO can be explained by an increase in the amount of reactive surface lattice oxygen.

References


A reaction path analysis of the catalytic partial oxidation of methane by transient experiments


Oxygen pathways in the oxidative coupling of methane over magnesium oxide based catalysts


6

INVESTIGATION ON THE REACTION MECHANISM FOR THE PARTIAL OXIDATION OF METHANE TO SYNTHESIS GAS OVER PLATINUM

6.1 Introduction

Different mechanisms for the partial oxidation of methane to synthesis gas have been proposed in the literature. At a methane to oxygen feed molar ratio of 2, *i.e.* the stoichiometric feed ratio, and temperatures ranging from 973 K to 1173 K thermodynamic equilibrium was achieved on 10 wt % refractory supported Ni (Prettre et al., 1946), mixed metal oxides of Ru (Ashcroft et al., 1990), various supported transition metals (Vernon et al., 1990; Vernon et al., 1992) and 25 wt. % Ni/Al$_2$O$_3$ (Dissanayake et al., 1991). On these catalysts the reaction is generally considered to occur in two stages (Prettre et al., 1946; Ashcroft et al., 1990; Dissanayake et al., 1991). First CH$_4$ is oxidised to CO$_2$ and H$_2$O. At the stoichiometric feed ratio for synthesis gas production O$_2$ is the limiting reactant and is completely converted. Next synthesis gas is produced via secondary reactions, either the steam and CO$_2$ reforming reactions (Prettre et al., 1946; Dissanayake et al., 1991) or the steam reforming and reverse water-gas shift reactions (Ashcroft et al., 1990). Baerns and coworkers postulated that CO$_2$ is formed as a primary product and that the formation of CO proceeds via a fast reaction of surface carbon species with CO$_2$, *i.e.* the reversed Boudouard reaction, on 1 wt. % Rh/γ-Al$_2$O$_3$. Furthermore, OH groups in the support are also involved in the CH$_x$ conversion to CO via a reforming reaction (Buyevskaya et al., 1994; Walter et al., 1994). Selectivities to CO and H$_2$ higher than equilibrium values on NiO-CaO (Choudhary et al., 1992A), 18.7 wt. % Ni/Al$_2$O$_3$ (Choudhary et al.,
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1993), Ni/Yb$_2$O$_3$ (Choudhary et al., 1992B), CoO/rare earth oxides (Choudhary et al., 1992C) and Co/MgO (Choudhary et al., 1992D) at temperatures lower than 973 K and a residence time of $10^{-2}$ s are attributed by the authors to primary formation of synthesis gas. However, Lunsford and co-workers attribute this observation to a hot spot in the catalyst bed, i.e. to a difference between the measured and the actual reaction temperature (Dissanayake et al., 1993). Schmidt and co-workers (Hickman and Schmidt, 1992, 1993A, 1993B; Hickman et al., 1993) reported CO and H$_2$ as primary products applying adiabatically operated Pt and Rh coated monoliths at outlet temperatures around 1300 K and residence times between $10^{-4}$ and $10^{-2}$ s. Simulations, based on a model of 19 elementary reaction steps, provided a theoretical basis for this observation (Hickman and Schmidt, 1993B). Lapszewicz and Jiang (1992) concluded that CO and CO$_2$ are produced in parallel over transition metal(s) supported on metal oxide(s) in the temperature range of 873 K to 1173 K. A similar mechanism is suggested by Matsumura and Moffat (1994) using a 10 wt. % Ru/SiO$_2$ catalyst.

The nature and reactivity of different oxygen forms on platinum has been investigated by various authors. Adsorbed atomic oxygen predominates between 150 and 500 K (Gland et al., 1980; Gland, 1980; Campbel et al., 1981; Derry and Ross, 1984). The incorporation of oxygen occurs between 800 and 1200 K (Kikuchi et al., 1974; Flynn and Wanke, 1975; Ducros and Merrill, 1976; Légaré et al., 1977; Matsushima et al., 1977; Gland et al., 1980; Niehus and Comsa, 1980) and two different forms are reported. The first is dissolved or subsurface atomic oxygen (Kikuchi et al., 1974; Flynn and Wanke, 1975; Engel and Ertl, 1979; Rotermund et al., 1993; Lauterbach et al., 1993; Lauterbach et al., 1994) and the second concerns platinum oxide, either PtO (Ducros and Merrill, 1976) or PtO$_2$ (Carrière et al., 1974; Légaré, et al., 1977; Peuckert and Bonzel, 1984). The oxide can be several layers thick, with significant diffusion of oxygen atoms into the bulk (Melmed, 1965; Lang et al., 1975; Nandi et al., 1982). Three different states of oxygen on platinum were also reported during the oxidation of CO between 300 and 700 K (Vishnevskii and Savchenko, 1989; Rotermund, 1993). The reactivity of clean and oxidised Pt towards the adsorption of H$_2$ and CO is different (McCabe and Schmidt, 1976, 1977). The oxidised Pt creates higher binding energy states for both H$_2$ and CO, with a change in the initial sticking coefficient. Impurities, particularly Si, segregate to the surface and become oxidised at approximately 1000 K leading to the formation of an oxide phase, which seems non-reactive towards CO and H$_2$ (Bonzel et al., 1981; Niehus and Comsa, 1981).

The objective of the study presented in this chapter is to investigate the reaction mechanism of the partial oxidation of methane over platinum and the role of different oxygen species.
6.2 Experimental procedures and definitions

The catalyst applied was platinum sponge with a grain size of 0.25 to 0.35 mm and its characterisation is reported in section 2.5.2.1. Non porous α-Al₂O₃ was used as inert packing material with a grain size of 0.25 mm to 0.30 mm. The inconel microreactor was charged with 0.20 g of catalyst and packed with inert material at each end. The catalyst has two important advantages for the present study. Firstly, no support is used to avoid interactions between platinum and a support material. Secondly, internal pore diffusion limitations can be neglected, which ensures a more reliable data evaluation.

Blank pulse experiments of pure oxygen, pure methane as well as methane and oxygen over α-Al₂O₃ showed a conversion of two percent, which is negligible compared to conversions obtained in the presence of a catalyst.

The amount of surface platinum atoms was determined in-situ by a multipulse experiments of oxygen at a temperature of 373 K over a surface covered with carbon monoxide, see section 2.5.2.1. The amount of platinum oxide was determined in-situ by a multipulse reduction with hydrogen. The response of water was measured from which the amount of incorporated oxygen was deduced. The catalyst pretreatment is discussed in section 2.5.2.2. Furthermore, prior to each experiment the catalyst was treated at reaction temperature with a steady flow of oxygen, unless mentioned otherwise, after which it was kept under a pressure of 10⁻⁵ Pa during 10 minutes.

In all experiments argon was added to the admitted gases as a reference component for calculation of the amount of admitted molecules and of the conversion of the reactants. The number of methane molecules admitted per pulse amounted to 10¹⁵ - 10¹⁶, resulting in an average total pressure of 100 Pa above the catalyst surface during 100 ms. Gas phase reactions can be neglected under these conditions. The ratio of admitted methane molecules in a single pulse to the theoretical number of surface platinum atoms was 0.05. During a multipulse experiment of oxygen 1 10¹⁶ molecules were admitted per pulse.

Temperatures ranging from 973 K to 1073 K were investigated. The detected reaction products were H₂, H₂O, CO and CO₂. No formation of ethane or ethene was observed.
For each experiment the conversion and selectivities as well as the carbon, hydrogen and oxygen balance were calculated, according to the following equations:

\[ X_{CH_4} = \frac{n_{in,CH_4} - n_{out,CH_4}}{n_{in,CH_4}} \tag{6.1} \]

\[ S_{H_2} = \frac{n_{out,H_2}}{n_{out,H_2} + n_{out,H_2O}} \tag{6.2} \]

\[ S_{CO} = \frac{n_{out,CO}}{n_{out,CO} + n_{out,CO_2}} \tag{6.3} \]

\[ \varepsilon_C = \frac{n_{out,CH_4} + n_{out,CO} + n_{out,CO_2}}{n_{in,CH_4}} \tag{6.4} \]

\[ \varepsilon_O = \frac{2n_{out,O_2} + 2n_{out,CO} + 2n_{out,CO_2} + n_{out,H_2O}}{2n_{in,O_2}} \tag{6.5} \]

\[ \varepsilon_H = \frac{4n_{out,CH_4} + 2n_{out,H_2} + 2n_{out,H_2O}}{4n_{in,CH_4}} \tag{6.6} \]

where \( n \) is the total number of moles (mol), \( X \) is the conversion (mol mol\(^{-1}\)), \( S \) is the selectivity (mol mol\(^{-1}\)) and \( \varepsilon \) is the mass balance (mol mol\(^{-1}\)). The subscript "in" means introduced into the reactor and the subscript "out" means detected at the reactor outlet.

The carbon and hydrogen balance mostly showed an accuracy better than 7 %. Errors up to 10 % are considered to be acceptable due to the accuracy of the absolute calibration factor. The conversion of methane was always nearly complete, unless specified otherwise.
6.3 Results and discussion

6.3.1 Interaction of oxygen with the catalyst

Following the review by Engel and Ertl (1979), the three different forms of oxygen reported in the introduction are referred to as platinum oxide, dissolved oxygen and chemisorbed oxygen species. The interaction of oxygen with the catalyst was investigated by multipulse experiments. In this case the catalyst was completely reduced prior to the experiment. Initially oxygen was not detected quantitatively, i.e. all oxygen molecules are incorporated by the catalyst. This uptake of oxygen is attributed to the formation of platinum oxide. The formation of an oxide phase is not expected from thermodynamic point of view at a typical pressure of 1-1000 Pa during the oxygen multipulse experiment, see section 3.2.3. Platinum oxide in the form of PtO or PtO$_2$ could also not be detected by an ex-situ XRD analysis, but the amount is in the range of the detection limit. However, formation of PtO (Ducros and Merrill, 1976) and PtO$_2$ (Carrière et al., 1974; Légare et al., 1977; Peuckert and Bonzel, 1984) is reported by interaction of platinum single crystal surfaces with oxygen at pressures between 1 Pa and 10$^5$ Pa at temperatures between 800 K and 1200 K. For the present study, at a temperature of 1023 K the amount of platinum oxide formed was equivalent to 6 wt. % PtO$_2$ or 900 theoretical monolayers of atomic oxygen.

The responses of a subsequent multipulse experiment are shown in Figure 6.1. The surface area of the oxygen responses increases for the first pulses to remain subsequently constant. The initial lower oxygen responses are due to oxygen interacting strongly with the catalyst, which is assigned to the presence of dissolved oxygen. The total amount of dissolved oxygen, as derived from the oxygen balance during the multipulse experiments, is equivalent to 0.7 theoretical monolayers of atomic oxygen at a temperature of 973 K and increases to 2.5 theoretical monolayers at a temperature of 1073 K. After a time interval of five minutes at 10$^5$ Pa this second type of oxygen species is completely removed. Five minutes is too long for the amount of dissolved oxygen involved to cause a signal above the noise level. The platinum oxide was stable during a period of at least several hours, as indicated by the constant oxygen balances of multipulse experiments carried out from time intervals of five minutes onwards up to two hours.

The peak maximum of each individual response of oxygen shifts to a larger time value than the peak maximum of the argon response, see Figure 6.2, also for the initial lower oxygen responses. This points to a third type of oxygen species interacting with the catalyst, which is also present when the amount of dissolved
oxygen has not reached its maximum value. This species, assigned as dissociatively chemisorbed oxygen, desorbs completely within two seconds, as expected from a typical activation energy for desorption of 217 kJ mol\(^{-1}\) (Hickman and Schmidt, 1993B).

**Figure 6.1:** Response of oxygen as a function of time. Multipulse experiment of oxygen at 973 K.

**Figure 6.2:** Normalised responses of argon (x 4.5) and oxygen as a function of time. Pulse experiment of oxygen and argon (10 vol. %) at 1023 K.

### 6.3.2 Interaction of methane with the reduced catalyst

The interaction of methane with the catalyst was investigated by introducing
Investigation on the reaction mechanism for the partial oxidation of methane to synthesis gas over platinum

a single pulse of methane. In this case the catalyst was completely reduced prior to the experiment. The residence time of methane amounted to 0.2 s and that of hydrogen to 0.4 s. No formation of carbon monoxide, carbon dioxide, ethane and ethene was observed. The carbon balance was significantly negative, whereas the hydrogen balance was closed within 5 % or less, indicating that formation of surface carbon occurred. The conversion of methane increased from 47 % at a temperature of 944 K to 82 % at 1023 K. The overall activation energy for the methane decomposition amounted to 52 kJ mol⁻¹, which is in good agreement with values reported for transition metal surfaces (Kuijpers et al., 1981; Lee et al., 1986; Beckerle et al., 1987; Brass and Ehrlich, 1987A; Brass and Ehrlich, 1979B; Anderson and Maloney, 1988).

6.3.3 Interaction of methane with platinum oxide and dissolved oxygen

The interaction of methane with platinum oxide and dissolved oxygen was investigated with pulse experiments of methane alone. Pulsing of methane was started at a time interval of either 10 s or 10 minutes after the treatment with oxygen. In the latter case only oxygen in the form of platinum oxide is available, whereas in the former also dissolved oxygen species are present.

![Figure 6.3: Normalised responses of CH₄ (x 46), CO (x 1.3), CO₂ (x 1.2), H₂ and H₂O (x 1.5) as a function of time. Methane pulse experiment at 1023 K, 10 min. after the oxygen treatment.](image-url)
The normalised responses of CH$_4$, CO, CO$_2$, H$_2$ and H$_2$O when pulsing methane 10 minutes after the treatment with O$_2$ are shown in Figure 6.3. H$_2$ is observed earlier than H$_2$O and CO earlier than CO$_2$. These results show that CO is the primary carbon containing and H$_2$ is the primary hydrogen containing product on platinum oxide. This was confirmed by a multipulse experiment of methane at similar conditions. Totally $5 \times 10^{18}$ molecules were introduced into the reactor, after which 95 % of the 900 theoretical monolayers of atomic oxygen initial present are converted. The conversion of methane decreased from 95 to 64 %, while the selectivities to CO and H$_2$ increased from 45 % and 39 % to 100%.

Applying the time interval of 10 s after the treatment with oxygen the reaction pathways depend on the dissolved oxygen concentration. The latter was varied by admitting an adapted amount of methane prior to the experiment. Figure 6.4 shows the normalised responses of CH$_4$, CO, CO$_2$, H$_2$ and H$_2$O when prior to the experiment 5 % of the dissolved oxygen was removed. The response of CO$_2$ has two maxima. The first maximum is observed before that of CO, which means that CO$_2$ is a primary product. The direct formation of CO$_2$ involves dissolved oxygen species. The formation of CO is attributed to the interaction of methane with oxygen present as platinum oxide. CO$_2$ is also a secondary product from CO as should be concluded from the second maximum in the CO$_2$ response. Both H$_2$O and H$_2$ are primary products, since H$_2$O is observed earlier than H$_2$.

![Figure 6.4: Normalised responses of CH$_4$ (x 59), CO (x 2.1), CO$_2$ (x 8.3), H$_2$ and H$_2$O (x 3.1) as a function of time. Methane pulse experiment at 1023 K, 10 s after the oxygen treatment. Prior to the experiment 5 % of the dissolved oxygen was removed.](image)
It is concluded that parallel reaction paths exist for the formation of CO and CO\textsubscript{2} as well as for H\textsubscript{2} and H\textsubscript{2}O by involvement of different forms of oxygen.

6.3.4 Interaction of methane with chemisorbed oxygen species and vice versa

The role of chemisorbed oxygen species was investigated with alternating pulse experiments of oxygen and methane and vice versa. A methane to oxygen feed molar ratio of 0.5 was used to ensure complete reoxidation of the catalyst. Nine different time intervals were applied. The oxygen balances were reasonable in all cases.

Firstly, an experiment starting with oxygen was carried out. Chemisorbed oxygen species created during the first pulse are completely desorbed after a time interval of 2 s. Varying the time interval between the two pulses from zero up to 2 s resulted in an increase in the selectivity to CO from 1 to 7 %. The corresponding selectivity to H\textsubscript{2} increased from 4 to 18 %. These results show that chemisorbed oxygen species are involved in non-selective reaction paths. At a time interval of 9 s the selectivities to CO and H\textsubscript{2} amounted to 17 and 26 % due to the disappearance of dissolved oxygen.

Secondly, an experiment starting with methane was performed, the time interval being varied between zero and 0.5 s. The selectivity to CO increased from 2 to 16 % and the corresponding value for H\textsubscript{2} from 4 to 24 %. Figure 6.5 shows the normalised responses of CH\textsubscript{4}, CO, CO\textsubscript{2}, H\textsubscript{2} and H\textsubscript{2}O at a time interval of 0.03 s. The responses of CO\textsubscript{2} and H\textsubscript{2}O show two maxima. Carbon dioxide is a primary product, since the first maximum in the CO\textsubscript{2} response is observed before the response of CO. As soon as oxygen is introduced the formation of CO\textsubscript{2} increases, resulting in a second maximum, while the formation of CO abruptly decreases.

A similar behaviour appears from the responses of H\textsubscript{2}O and H\textsubscript{2}. These observations indicate that chemisorbed oxygen species catalyse the consecutive oxidation of CO and H\textsubscript{2}.

In the case of a time interval of 0.5 s the oxygen was introduced when gaseous methane was not present anymore in the catalyst bed. No formation of carbon containing reaction products was observed during the interaction of oxygen with the surface, which means that long living reactive carbon species are not present at the surface.
A reaction path analysis of the catalytic partial oxidation of methane by transient experiments

Figure 6.5: Normalised responses of CH₄ (x 33), CO (x 2.6), CO₂ (1.2), H₂ (x 1.8) and H₂O as a function of time. Alternating pulse experiment starting with methane followed by oxygen at a time interval of 0.03 s. Methane to oxygen feed molar ratio of 0.5 and a temperature of 1023 K.

6.3.5 Simultaneous interaction of methane and oxygen with the catalyst

The simultaneous interaction of methane and oxygen with the catalyst was investigated by pulse experiments at a stoichiometric feed ratio. Oxygen was not detected quantitatively, i.e. all oxygen molecules are converted. The selectivities to CO and H₂ as well as the oxygen balances are shown in Table 6.1. The excess in the oxygen balances indicates that oxygen present as platinum oxide is incorporated into the reaction products. The selectivities to hydrogen and carbon monoxide decrease at increasing reaction temperature.

Table 6.1: Selectivities to CO and H₂ and oxygen balances when methane and oxygen are pulsed simultaneously at a stoichiometric feed ratio.

<table>
<thead>
<tr>
<th>T / K</th>
<th>S_{CO} / %</th>
<th>S_{H₂} / %</th>
<th>\varepsilon_{O} / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>973</td>
<td>46</td>
<td>62</td>
<td>204</td>
</tr>
<tr>
<td>1023</td>
<td>42</td>
<td>51</td>
<td>320</td>
</tr>
<tr>
<td>1073</td>
<td>31</td>
<td>30</td>
<td>370</td>
</tr>
</tbody>
</table>
Investigation on the reaction mechanism for the partial oxidation of methane to synthesis gas over platinum

A reasonable oxygen balance was obtained by admitting an adapted amount of methane prior to the experiment at a temperature of 1023 K. The selectivity to CO and H₂ increased to 69 and 88%. The normalised responses of CH₄, CO, CO₂, H₂ and H₂O are shown in Figure 6.6. The shape of the normalised responses of CO and H₂ is nearly identical. The response of H₂ is observed before H₂O, which means that H₂ is a primary product. CO₂ is observed later than CO, indicating that CO is a primary product.

A pulse experiment with a stoichiometric feed ratio performed over a reduced catalyst showed no significant formation of CO and CO₂. The oxygen is incorporated into the catalyst, which indicates that platinum oxide has to be present for the formation of synthesis gas. This point is further addressed in Chapter 7 for both platinum and rhodium sponge as catalyst. The carbon adatoms remain adsorbed on the surface and were removed applying a continuous flow of oxygen.

![Figure 6.6: Normalised responses of CH₄ (x 6.4), CO (x 1.1), CO₂ (2.4), H₂ and H₂O (x 5.3) as a function of time. Simultaneous pulse experiment of methane and oxygen at 1023 K and a stoichiometric feed ratio. The catalyst was partly reduced by methane prior to the experiment.](image)

The incorporation of oxygen present as platinum oxide in the reaction products was verified by simultaneous pulsing of CH₄ and ¹⁸O₂ at a stoichiometric feed ratio. During the first pulses C¹⁶O, C¹⁶O¹⁸O, C¹⁸O₂, H₂¹⁶O and H₂¹⁸O were produced, but formation of C¹⁸O and C¹⁸O₂ was not observed. CO is only produced via ¹⁶O oxygen present in the form of platinum oxide. Chemisorbed oxygen species are only incorporated into CO₂ in the form of C¹⁶O¹⁸O, which
confirms their role in the consecutive oxidation of CO. The percentage of $^{18}$O$_2$ oxygen incorporated into the reaction products only amounts to 3 %, the major oxidation products being C$^{18}$O$_2$ and H$_2^{16}$O. The reaction mainly proceeds via oxygen present as platinum oxide, while the gaseous oxygen reoxidises the catalyst.

Finally, the carbon balances indicate that no deposition of carbon occurred during the interaction of methane with a partly oxidised catalyst. XPS and EDS studies on a used catalyst could not reveal the presence of carbon.

6.3.6 Reaction mechanism

The reaction network of the partial oxidation of methane to synthesis gas over platinum is illustrated in Figure 6.7.

![Figure 6.7: Reaction network for the partial oxidation of methane to synthesis gas in the presence of oxygen over platinum sponge at temperatures between 973 K and 1073 K. Partially reduced PtO$_x$ is reoxidised by dioxygen.](image)

Methane dissociates on reduced platinum to surface carbon and hydrogen adatoms. No deposition of carbon occurs during the interaction of methane or methane/oxygen with a partly oxidised catalyst. Reactive carbon species with a long life time are not present either at the surface.

A physical picture of a platinum surface consisting of a matrix of metallic platinum and islands of an oxide phase seems in line with literature results. The existence of a solid mixed phase containing PtO$_2$ as well as Pt was reported by Peuckert and Bonzel (1984), who studied the decomposition of platinum oxide under ultra high vacuum conditions. This phase seems stable up to a temperature of 1100 K. Niehus and Comsa (1980) reported that the platinum oxide phase of
Investigation on the reaction mechanism for the partial oxidation of methane to synthesis gas over platinum

oxidised platinum is stable up to 1300 K. The formation of dissolved oxygen species is believed to occur in the metallic platinum phase, in line with results reported by Lauterbach et al. (1993, 1994).

The direct formation of CO from methane occurs via oxygen present as platinum oxide, which also favours the recombination of two hydrogen adatoms to produce H₂. In parallel to this reaction, methane is directly converted to CO₂ and H₂O by involvement of dissolved oxygen. This involvement requires segregation of the dissolved oxygen species to the surface, where it reacts with methane. In this case the dissolved oxygen acts as a reservoir for chemisorbed oxygen, but a type with a reactivity different from that of the species already referred to as chemisorbed oxygen. Rigas et al. (1993) suggest that dissolved oxygen species modify the electronic properties of the surface and thus change the reactivity of adsorbed oxygen species for the ethylene epoxidation on silver powder. A mechanism for oxygen segregation is proposed by Lauterbach et al. (1994), who studied the reaction between subsurface oxygen and CO as well as H₂ on Pt(100). The reaction is assumed to occur on the border between the subsurface oxygen region and the surrounding region where CO or H₂ is adsorbed. In this region the subsurface platinum phase is restructured and this process uncovers subsurface oxygen atoms, which in turn react with the chemisorbed CO or H₂.

The consecutive oxidation of CO and H₂ occurs via oxygen present as platinum oxide and via chemisorbed oxygen species. For platinum oxide the consecutive reaction is more pronounced at increasing temperature.

In the presence of both methane and oxygen at a stoichiometric feed ratio the dominant reaction pathways are the direct formation of CO and H₂ followed by the consecutive oxidation to CO₂ and H₂O. The reaction proceeds via a redox cycle mechanism proposed by Mars and van Krevelen (1954) for selective oxidation reactions. The oxidation of methane is accompanied by the reduction of platinum oxide, which is reoxidised by incorporation of dioxygen into the catalyst.

6.4 Conclusions

Three different oxygen forms, corresponding to dissociatively chemisorbed oxygen, dissolved oxygen and platinum oxide are present during the interaction of dioxygen with platinum sponge. The maximum amount of platinum oxide is equivalent to 6 wt. % PtO₂. The decomposition of methane on reduced platinum results in the formation of surface carbon and hydrogen. Carbon monoxide and carbon dioxide are produced in parallel from methane by involvement of different oxygen species.
A reaction path analysis of the catalytic partial oxidation of methane by transient experiments

In the presence of both methane and oxygen at a stoichiometric feed ratio the dominant reaction pathways are the direct formation of CO and H\textsubscript{2} followed by their consecutive oxidation. A Mars-van Krevelen redox cycle is postulated for the partial oxidation of methane over platinum.

References


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Investigation on the reaction mechanism for the partial oxidation of methane to synthesis gas over platinum


A reaction path analysis of the catalytic partial oxidation of methane by transient experiments


7.1 Introduction

Synthesis gas, a mixture of CO and H₂, is used as feedstock for many important industrial processes, such as methanol production or the Fischer-Tropsch process. Presently, the most important industrial route to synthesis gas is steam-reforming of methane. A promising alternative for the production of synthesis gas is the partial oxidation of methane over supported transition metals due to the more favourable H₂ to CO ratio in the product gas as well as the mild exothermicity of the reaction.

Prettre et al. (1946) were among the first to report formation of synthesis gas by catalytic conversion of CH₄/O₂ mixtures at a stoichiometric feed ratio, i.e. a methane to oxygen feed molar ratio of 2, over 10 wt. % refractory supported Ni at temperatures in the range of 973 K to 1173 K. Thermodynamic equilibrium was achieved under all conditions studied, corresponding to the catalyst bed exit temperature. The reaction was reported to occur in two stages. In the first stage methane is converted to CO₂ and H₂O until complete conversion of oxygen is achieved, since oxygen is the limiting reactant at a stoichiometric feed ratio. In the second stage synthesis gas is produced via secondary reactions such as the carbon dioxide and steam reforming reaction.

A similar mechanism has been proposed for the partial oxidation of methane over mixed metal oxides of Ru (Ashcroft et al., 1990), various supported transition
metals (Vernon et al., 1990, 1992), 25 wt. % Ni/Al₂O₃ (Dissanayake et al., 1991) and various supported nickel catalysts (Vermeiren et al., 1992).

Baarns and coworkers (Buyevskaya et al., 1994; Walter et al., 1994) investigated the partial oxidation of methane over 1 wt. % Rh/γ-Al₂O₃ at a temperature of 1000 K. A surface carbon species and CO₂ are postulated to be the primary reaction products formed by the reaction of methane with reduced and oxidised surface sites. Formation of CO proceeds via a fast reaction between surface carbon species and CO₂, i.e. the reversed Boudouard reaction. Furthermore, OH groups on the support are also considered to be involved in the CHₓ conversion to CO via a reforming reaction.

Choudhary et al. (1992A, 1992B, 1992C, 1992D, 1993) report selectivities to synthesis gas higher than the values predicted by thermodynamic equilibrium in the partial oxidation of methane over NiO-CaO, 18.7 wt. % Ni/Al₂O₃, Ni/Yb₂O₃, CoO/rare earth oxides and CoO/MgO at temperatures lower than 973 K and a residence time of 10⁻² s. The authors attribute this observation to primary formation of synthesis gas. However, Dissanayake et al. (1993) report that a difference between the measured and the actual reaction temperature also provides an explanation for the observed difference in selectivities.

Formation of CO and H₂ as primary reaction products in the partial oxidation of methane is reported by Schmidt and co-workers (Hickman and Schmidt, 1992, 1993A, 1993B; Hickman et al., 1993) applying adiabatically operated monoliths containing a platinum or rhodium catalyst at outlet temperatures around 1300 K and residence times between 10⁻⁴ and 10⁻² s. Simulations carried out on the basis of a model consisting of nineteen elementary reaction steps provided a theoretical basis for this observation (Hickman and Schmidt, 1993B).

Parallel formation of CO and CO₂ during the partial oxidation of methane is reported by Lapszewicz and Jiang (1992) for transition metal(s) supported on metal oxide(s) and Matsumura and Moffat (1994) applying a 10 wt. % Ru/SiO₂ catalyst.

The interaction of dioxygen with rhodium and the formation of an oxide phase is of interest in the partial oxidation of methane. Formation of Rh₂O₃ is reported by various authors during the treatment of rhodium with dioxygen or air at various pressures and temperatures. Salanov and Savchenko (1993A, 1993B, 1993C, 1994) investigated the interaction of oxygen with Rh(100) and polycrystalline rhodium. At oxygen pressures below 10⁻⁵ Pa and temperatures between 400 K and 1600 K oxygen can occur in various states, depending on the surface coverage (Salanov and Savchenko, 1993A, 1993B): chemisorbed on the surface, penetrated into the near-surface layer of the metal and as part of surface oxide islands. At oxygen pressures higher than 0.1 Pa up to 1000 Pa and temperatures between 400 K and 600 K formation of a bulk Rh₂O₃ phase is reported (Salanov and Savchenko, 1993C, 1994). Peuckert (1984) studied the
The reaction mechanism of the partial oxidation of methane to synthesis gas: a transient kinetic study over rhodium and a comparison with platinum

oxidation of polycrystalline rhodium at 870 K and an oxygen pressure of $10^5$ Pa. The surface was analysed by means of X-ray Photoelectron Spectrometry and it was concluded that a Rh$_2$O$_3$ phase was formed. Wang and Schmidt (1981) investigated the surface composition of rhodium particles on planar amorphous SiO$_2$ following treatment at atmospheric pressure and various temperatures in air or H$_2$. A complete oxidation to Rh$_2$O$_3$ is reported as a result of a treatment with air at 773 K. The oxidation kinetics of rhodium in air at $10^5$ Pa in the temperature range of 873 K to 1273 K was studied by Carol and Mann (1990) and formation and growth of Rh$_2$O$_3$ was reported. Two structures, a hexagonal and orthorhombic crystal structure, control the nature of the oxidation kinetics. Beck et al. (1993) studied changes in the local structure of rhodium oxide particles in a Rh/Al$_2$O$_3$ catalyst caused by treatment in dioxygen at atmospheric pressure and temperatures in the range of 800 K to 1400 K. A complete oxidation of rhodium to Rh$_2$O$_3$ was reported at temperatures at or above 800 K and the Rh$_2$O$_3$ particles have a structure similar to orthorhombic Rh$_2$O$_3$. Kellog (1985, 1986) reported formation of stoichiometric Rh$_2$O$_3$ on rhodium surfaces at temperatures of 500 K and higher at an oxygen pressure of 130 Pa.

The reduction characteristics of Rh$_2$O$_3$ are also of interest. According to Peuckert (1984) the decomposition of the Rh$_2$O$_3$ phase proceeds via a mixed phase of metallic rhodium and Rh$_2$O$_3$. Treatment of Rh$_2$O$_3$ particles in hydrogen at 423 K results in complete reduction to rhodium metal, as reported by Wang and Schmidt (1981). Rh$_2$O$_3$ was also reduced by CO at a pressure of 133 Pa at temperatures above 420 K, as reported by Kellog (1986). Oh and Carpenter (1983) investigated the oxidation state of rhodium following pretreatment with several gases between 500 K and 800 K. The oxidation state of supported rhodium changed reversibly in response to a change in the stoichiometry of its gaseous environment. The catalyst surface was observed to consist mainly of Rh$_2$O$_3$ in a net-oxidising environment, while in the case of a net-reducing stream mainly metallic rhodium is present.

The objective of the study presented in this chapter is to investigate the reaction mechanism of the partial oxidation of methane to synthesis gas over rhodium. Both the separate and the simultaneous interaction of methane and dioxygen with the catalyst as well as the reactivity of different oxygen species in the partial oxidation of methane was studied. The emphasis was put on obtaining information concerning these phenomena on a catalyst which was at steady-state with an environment as typical as possible for the partial oxidation: i.e. a temperature of 1100 K and a gas phase consisting of methane and oxygen in a feed molar ratio of 2. The reaction paths are analysed in terms of primary and secondary product formation and a detailed reaction mechanism is proposed.
Knudsen diffusion, combined with adsorption and desorption processes are simulated by integrating the continuity equations for the reaction products in order to avoid interference of the latter with the reaction network analysis. The results are compared to previous work involving platinum as the catalyst (Mallens et al., 1995).

7.2 Experimental procedures and definitions

The catalysts applied were rhodium sponge and platinum sponge. Non-porous \( \alpha \)-Al\(_2\)O\(_3\) with a grain diameter of 0.25 mm to 0.30 mm was used as inert packing material. The catalyst has two important advantages for the present study. No support is used to avoid interactions between the metal and a support material as well as interactions between reactants or reaction products and a support material. Secondly, the time scale for Knudsen diffusion in the interstitial voids is one hundred times the time scale of Knudsen diffusion in the intragranular voids. This means that the shape of the response is not influenced by intragranular diffusion (Huinink, 1995). The inconel microreactor, was charged with 0.07 to 0.2 g of catalyst and packed with inert material at each end. Blank pulse experiments of pure oxygen, pure methane as well as methane with oxygen over \( \alpha \)-Al\(_2\)O\(_3\) showed a conversion of two percent, which is negligible compared to conversions obtained in the presence of a catalyst.

The number of molecules admitted per single pulse was in the range of \( 10^{15} - 10^{16} \), resulting in an average total pressure of 100 Pa above the catalyst surface during 100 ms. Gas phase reactions can be neglected under these conditions. In a single pulse the ratio of admitted methane as well as oxygen molecules to the theoretical number of surface rhodium atoms was always below 0.05. In all experiments argon was added to the admitted gases as a reference component for calculation of the conversion of the reactants and the amount of admitted molecules.

The amount of surface metal atoms and of metal oxide was determined in-situ. The former followed from a multipulse experiment of oxygen at a temperature of 373 K over a surface covered with carbon monoxide, see section 2.5.2.1. The amount of metal oxide was determined by both a steady flow and a multipulse reduction with hydrogen. The response of water was measured from which the amount of incorporated oxygen was deduced. In case of a multipulse experiment typically 200 pulses of hydrogen were introduced, during which the number of molecules per pulse is in the range of \( 10^{16} - 10^{17} \). In both cases the experiment was continued until the water production was negligible. Integration of the water response yields the total amount of atomic oxygen present as metal oxide.
The reaction mechanism of the partial oxidation of methane to synthesis gas: a transient kinetic study over rhodium and a comparison with platinum

Repetition of a multipulse reduction at various time intervals after the experiment did not show water formation, from which it was concluded that complete reduction had occurred. The catalyst was pretreated in-situ, as described in section 2.5.2.2. Furthermore, prior to each transient experiment the catalyst was treated with a steady flow of methane and oxygen, unless mentioned otherwise, in the same feed molar ratio as the following experiment, after which it was kept under a pressure of $10^{-5}$ Pa during five minutes.

The experiments were carried out in the temperature range of 873 K to 1023 K. The detected reaction products were $\text{H}_2$, CO, $\text{H}_2\text{O}$ and $\text{CO}_2$. No formation of $\text{C}_2$ products was observed. For each experiment the conversion and selectivities as well as carbon, hydrogen and oxygen balance were calculated, according to the following equations:

$$X_{\text{CH}_4} = \frac{n_{\text{in},\text{CH}_4} - n_{\text{out},\text{CH}_4}}{n_{\text{in},\text{CH}_4}}$$  \hspace{1cm} (7.1)

$$s_{\text{H}_2} = \frac{n_{\text{out},\text{H}_2}}{n_{\text{out},\text{H}_2} + n_{\text{out},\text{H}_2\text{O}}}$$  \hspace{1cm} (7.2)

$$s_{\text{CO}} = \frac{n_{\text{out},\text{CO}}}{n_{\text{out},\text{CO}} + n_{\text{out},\text{CO}_2}}$$  \hspace{1cm} (7.3)

$$\varepsilon_C = \frac{n_{\text{out},\text{CH}_4} + n_{\text{out},\text{CO}} + n_{\text{out},\text{CO}_2}}{n_{\text{in},\text{CH}_4}}$$  \hspace{1cm} (7.4)

$$\varepsilon_O = \frac{2n_{\text{out},\text{O}_2} + n_{\text{out},\text{CO}} + 2n_{\text{out},\text{CO}_2} + n_{\text{out},\text{H}_2\text{O}}}{2n_{\text{in},\text{O}_2}}$$  \hspace{1cm} (7.5)

$$\varepsilon_H = \frac{4n_{\text{out},\text{CH}_4} + 2n_{\text{out},\text{H}_2} + 2n_{\text{out},\text{H}_2\text{O}}}{4n_{\text{in},\text{CH}_4}}$$  \hspace{1cm} (7.6)

where $X$ is the conversion (mol mol$^{-1}$), $S$ is the selectivity (mol mol$^{-1}$), $n$ is the total amount of moles (mol) and $\varepsilon$ is the mass balance (mol mol$^{-1}$).
The carbon, hydrogen and oxygen balance always showed an accuracy better than 8%. Errors up to 10% are considered to be acceptable in view of the accuracy of the absolute calibration factor. The conversion of methane was always nearly complete, unless specified otherwise.

Apparent activation energies for the interaction of oxygen and methane with the catalyst were derived from the linear dependence of \( \ln X \) on the inverse temperature, applying an identical amount of molecules per pulse at various temperatures. Only experiments in which the conversion is lower than 50% were selected for determination of the activation energies.

7.3 Model equations for the simulation of adsorption, desorption and Knudsen diffusion processes

The outlet flow rates of the four reaction products at 973 K were calculated by integrating the corresponding continuity equations for a single pulse of an equimolar mixture of CO, CO\(_2\), H\(_2\) and H\(_2\)O and corresponding Knudsen diffusion, adsorption and desorption coefficients to investigate the influence of these processes on the shape of the responses. Reaction was not included in the simulations. Comparison of these simulation results to the results obtained by simultaneous pulsing of methane and oxygen allows to ascertain that the above phenomena do not disguise the reaction network analysis of the partial oxidation of methane to synthesis gas.

In general when studying a catalytic reaction with the TAP set-up, the microreactor will be packed with three subsequent beds. The response after injection of a gas pulse is a function of all processes appearing in the reactor: gas transport, adsorption, desorption and reaction, and can be simulated by integrating the continuity equations for all components considered. When the catalyst bed is placed in the isothermal part of the reactor, the energy balances can be omitted. In the present analysis, the only processes taken into consideration are diffusion, adsorption and desorption.

It is assumed that the only transport mechanism of molecules through the reactor is Knudsen diffusion. This assumption is valid since the amount of molecules per pulse was always below \( 10^{16} \) and under these conditions Knudsen diffusion is the dominant transport mechanism (Huinkink, 1995). The effective Knudsen diffusion coefficient of component A, is calculated as follows:
The reaction mechanism of the partial oxidation of methane to synthesis gas: a transient kinetic study over rhodium and a comparison with platinum

\[ D_{e,A}^K = \frac{\varepsilon_b d_i}{\tau_b} \frac{8RT}{3\pi M_A} \] (7.7)

where \( D_{e,A}^K \) is the effective Knudsen diffusion coefficient (m\(^3\) m\(^{-1}\) s\(^{-1}\)), \( \varepsilon_b \) is the bed porosity (m\(^3\) m\(^{-3}\)), \( \tau_b \) is the bed tortuosity (m\(^2\) m\(^{-2}\)), \( d_i \) is the diameter of the interstitial voids (m), \( R \) is the general gas constant (J mol\(^{-1}\) K\(^{-1}\)), \( T \) is the temperature (K) and \( M_A \) is the molecular mass (kg mol\(^{-1}\)). The diameter of the interstitial voids, \( d_i \), follows from the definition for the hydraulic diameter (Huizenga and Smith, 1986).

The continuity equations are shown for a general case of component A, showing first order adsorption and desorption:

\[ A + * \xrightarrow{k_{des}} \xrightarrow{k_{ads}} A * \] (7.8)

The gas phase concentration profile of component A as function of the reactor coordinate can be calculated by integrating the continuity equations for component A in each of the packed beds, \( i.e. \) two inert beds and one catalyst bed. Only the balances for the catalyst bed are presented here. In the case of the inert beds the reaction terms in the continuity equations can be put equal to zero.

The continuity equations for the gas phase component A and the corresponding adsorbed species over the catalyst bed, Equations 7.9 and 7.10, as well as the initial and boundary conditions are shown below.

\[ \varepsilon_b \frac{\partial C_A}{\partial t} = D_{e,A}^K \frac{\partial^2 C_A}{\partial x^2} + \left( 1 - \varepsilon_b \right) a_v L_i \left( -k_{ads} C_A \left( 1 - \Theta_A \right) + k_{des} \Theta_A \right) \] (7.9)

\[ \frac{\partial \Theta_A}{\partial t} = k_{ads} C_A \left( 1 - \Theta_A \right) - k_{des} \Theta_A \] (7.10)

The initial conditions, Equations 7.11 and 7.12, follow from the initial gas phase concentration and the initial surface coverage of component A:

\[ t = 0 \land 0 \leq x \leq l_b : C_A(x) = \delta_x \frac{N_{p,A}}{\varepsilon_b A_s} \] (7.11)

\[ t = 0 \land 0 \leq x \leq l_b : \Theta_A(x) = 0 \] (7.12)
The two boundary conditions are shown by Equations 7.13 and 7.14. After the introduction of the gas pulse, the pulse valve is closed meaning a zero flux at the reactor entrance:

\[ t \geq 0 \land x = 0: \frac{\partial C_A}{\partial x} = 0 \tag{7.13} \]

The concentration for component A at the end of the catalyst bed can be put equal to zero, because the reactor outlet is maintained at a pressure of \( 10^{-5} \) Pa:

\[ t \geq 0 \land x = l_b: C_A = 0 \tag{7.14} \]

where \( a_v \) is the external catalyst surface area per unit catalyst volume (\( m_c^2 m_c^{-3} \)), \( L_t \) is the maximal molar concentration per square meter catalyst surface (\( \text{mol} \ m_c^{-2} \)), \( C_A \) is the concentration (\( \text{mol} \ m_g^{-3} \)), \( \Theta \) is the fractional coverage on the surface (\( - \)), \( x \) is the axial reactor coordinate (\( \text{m} \)), \( t \) is the time (\( \text{s} \)), \( l_b \) is the bed length (\( \text{m} \)), \( k_{\text{ads}} \) is the adsorption rate coefficient and \( k_{\text{des}} \) is the desorption rate coefficient.

The partial differential equations with the accompanying initial and boundary conditions were integrated numerically with the routine D03PGF from the NAG Fortran Library, as described by Huinink (1995). The Knudsen diffusion coefficients were calculated using the relationship given by Equation 7.7. The values for the adsorption and desorption rate coefficients are obtained from Hickman and Schmidt (1993A), since these values are taken from studies on unsupported single crystals as well as polycrystalline catalyst studies. The adsorption and desorption of CO\(_2\) is neglected in their model.

The values for the parameters used in the simulations are shown in Appendix 7A. The results of the simulations at 973 K are shown in Figure 7.1, which shows the normalised responses of hydrogen, water, carbon monoxide and carbon dioxide when Knudsen diffusion, adsorption and desorption are considered. In this case the response of water is observed prior to that of hydrogen and the response of carbon dioxide is observed prior to that of carbon monoxide.
The reaction mechanism of the partial oxidation of methane to synthesis gas: a transient kinetic study over rhodium and a comparison with platinum

Figure 7.1: Normalised responses of $H_2$ (x 1.72), $H_2O$, CO (x 10.14) and $CO_2$ (x 1.59) as a function of time. Simulation of Knudsen diffusion, adsorption and desorption at 973 K over rhodium sponge by integrating continuity equations 7.9 and 7.10 with initial and boundary conditions 7.11-7.14 and parameter values given by Appendix 7A.

The shape of the responses can be explained qualitatively by comparison of the characteristic times of Knudsen diffusion, adsorption and desorption for hydrogen, water and carbon monoxide. These values are calculated by the following equations:

\[
\tau_{\text{diff}} = \frac{l_b^2 \varepsilon_b}{2 D_{e,A}^K} \tag{7.15}
\]

\[
\tau_{\text{ads}} = \frac{\varepsilon_b}{(1 - \varepsilon_b) a_v L_i k_a \Theta_v} \tag{7.16}
\]

\[
\tau_{\text{des}} = \frac{1}{k_{\text{des}}} \tag{7.17}
\]

where $\tau_{\text{diff}}$ is the characteristic time for Knudsen diffusion, $\tau_{\text{ads}}$ is the characteristic time for adsorption and $\tau_{\text{des}}$ is the characteristic time for desorption. The results at 973 K are shown in Table 7.1 for a total bed length of 25 $10^{-3}$ mm.
A reaction path analysis of the catalytic partial oxidation of methane by transient experiments

Table 7.1: Characteristic times for Knudsen diffusion, adsorption and desorption of various gases on rhodium sponge at a temperature of 973 K.

<table>
<thead>
<tr>
<th>Characteristic time</th>
<th>H₂</th>
<th>H₂O</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Knudsen diffusion / s</td>
<td>1.4 \times 10^{-2}</td>
<td>2.3 \times 10^{-2}</td>
<td>2.9 \times 10^{-2}</td>
</tr>
<tr>
<td>Adsorption / s</td>
<td>5.6 \times 10^{-9}</td>
<td>1.7 \times 10^{-8}</td>
<td>6.5 \times 10^{-9}</td>
</tr>
<tr>
<td>Desorption / s</td>
<td>2.2 \times 10^{-9}</td>
<td>2.7 \times 10^{-11}</td>
<td>3.1 \times 10^{-7}</td>
</tr>
</tbody>
</table>

In the case of hydrogen an adsorption equilibrium can be expected, which explains the broadening of the hydrogen response due to adsorption and desorption phenomena. For carbon monoxide the relative slow desorption from the surface causes the large broadening of the response. In the case of water the response resembles that determined by diffusion alone, because the equilibrium is on the side of gaseous water.

7.4 Experimental results

7.4.1 Interaction of oxygen with reduced rhodium

The interaction of oxygen with the catalytic surface was investigated with a steady flow experiment of oxygen as well as multipulse experiments of oxygen. The catalyst was exposed to a steady flow of oxygen at a temperature of 1073 K. In this case the catalyst was completely reduced prior to the experiment. Initially oxygen was not detected quantitatively, i.e. no breakthrough of oxygen was observed. Subsequently, the oxygen signal increased and finally a constant value was reached after a period of 2500 s. The argon response remained constant during this experiment. The initial low oxygen signals are attributed to the incorporation of oxygen into the catalyst and the ratio of incorporated atomic oxygen to the number of rhodium atoms can be calculated to be 1.7 from the oxygen balance.

A sample of the treated catalyst as well as the fresh rhodium sponge was analysed ex-situ by means of X-Ray Diffractometry (XRD) measurements as well as X-Ray Photoelectron Spectrometry (XPS) measurements. The fresh sample was in-situ reduced at 973 K by a steady flow of hydrogen during one hour. After this reduction the sample was cooled to room temperature maintaining a pressure of \(10^{-5}\) Pa. Finally, the sample was transferred to the XPS set-up for analysis.

The analysis of the treated sample showed that it consisted of stoichiometric \(\text{Rh}_2\text{O}_3\) as well as metallic rhodium, while the fresh sample consisted solely of
metallic rhodium. From the XPS measurements it was concluded that in the case of the treated sample stoichiometric $\text{Rh}_2\text{O}_3$ is present and that the ratio of oxidic atomic oxygen to rhodium atoms amounted to 1.7, which is identical to the value obtained from the steady flow experiments. For the fresh sample solely metallic rhodium was detected. During the steady flow of oxygen the average pressure of oxygen in the catalyst bed amounts to $10^4$ Pa. Thermodynamic calculations, section 3.2.3, show that at oxygen pressures of 250 Pa or higher a $\text{Rh}_2\text{O}_3$ phase is thermodynamically stable at the investigated temperature. Therefore, the incorporation of oxygen into the catalyst is attributed to the almost complete oxidation of rhodium to $\text{Rh}_2\text{O}_3$.

A possible explanation for the absence of any surface oxygen in case of the fresh sample after transfer in the open air, is the structure of the catalyst, consisting of non-porous particles forming the porous grain of 2 $\mu$m, instead of a supported rhodium catalyst. This may also explain the partial decomposition of the treated sample, since XRD analysis revealed the presence of both $\text{Rh}_2\text{O}_3$ and metallic rhodium. This partial decomposition does not influence the XPS measurements under the assumption that due to diffusion of oxygen to the surface the latter remains oxidised.

The treated catalyst sample was kept during a time interval varying between zero and 1800 s at a pressure of $10^{-5}$ Pa and a temperature of 898 K, after which multipulse experiments of oxygen were carried out. In a typical experiment fifteen pulses were introduced with a two second time interval between the pulses. A typical result is shown in Figure 7.2. The surface area of the individual oxygen responses increases for the first pulses to remain subsequently constant. The initial lower oxygen signals are attributed to oxygen incorporation into the catalyst. The amount of incorporated oxygen increases linearly with increasing time at $10^{-5}$ Pa up to 0.7 theoretical monolayers of atomic oxygen at 1800 s. No constant value was reached as in the case of platinum after maintaining $10^{-5}$ Pa during at least 300 s (Mallens et al., 1995). A second series of multipulse experiments was carried out at 900 s after interrupting the steady flow of oxygen but now at temperatures between 875 K and 948 K. The amount of incorporated oxygen increases exponentially, especially above 923 K, up to 5.1 theoretical monolayers of atomic oxygen at 948 K. The peak maximum of each individual response of oxygen shifts to a larger time value than the peak maximum of the argon response, see Figure 7.3, which points to reversible adsorption of oxygen at the catalyst surface. After a time interval of two seconds no desorption of dioxygen is observed any more.
A reaction path analysis of the catalytic partial oxidation of methane by transient experiments

Figure 7.2: Response of oxygen as a function of time. Multipulse experiment of oxygen at 873 K over almost completely oxidised rhodium sponge.

Figure 7.3: Normalised responses of argon (x 5) and oxygen as a function of time. Pulse experiment of oxygen and argon (10 vol. %) at 1023 K over almost completely oxidised rhodium sponge.
7.4.2 Interaction of methane with reduced rhodium

The interaction of methane with the catalyst was investigated by introducing a single pulse of methane. In this case the catalyst was completely reduced prior to the experiment. Methane and hydrogen responses were monitored at the reactor outlet. No formation of carbon monoxide, carbon dioxide, ethane and ethene was observed. The residence time of methane amounted to 0.2 s and that of hydrogen to 0.4 s. The carbon balance was significantly negative, whereas the hydrogen balance was closed within 7 % or less, indicating the formation of carbon adatoms. The conversion of methane increased from 44 % at 598 K to 81 % at 748 K. The apparent activation energy for methane decomposition amounted to 15 kJ mol⁻¹.

7.4.3 Alternating pulse experiments over rhodium

The role of adsorbed oxygen species was investigated with alternating pulse experiments of oxygen and methane and vice versa. A methane to oxygen molar ratio of 0.5 was used to ensure complete reoxidation of the catalyst. No oxygen was detected quantitatively, i.e. all oxygen molecules are converted, and the carbon as well as hydrogen balances were always closed. The oxygen balance was not closed at all time intervals applied and some oxygen was incorporated into the catalyst. However, this does not influence the experimental results since this amount is very small compared to the amount of Rh₂O₃ already present. Prior to the experiments the catalyst was treated with a steady flow of methane and oxygen with a molar feed ratio of 0.5 until a steady-state was reached. Product formation was only observed during the methane pulse.

First, an experiment starting with oxygen was carried out. Seven different time intervals between the oxygen and methane pulse were applied, varying from zero, i.e. simultaneous pulsing, up to 9 s. Figure 7.4 shows the selectivities to H₂ and CO as a function of the time interval between the oxygen and the methane pulse. The selectivity to CO increases from 7 % when pulsing simultaneously to 33 % at a time interval of 2 s, while the corresponding H₂ selectivity increases from 18 % to 58 %. The selectivities to CO and H₂ do not vary significantly when the time interval between the methane and oxygen pulse is further increased from 2 s up to 9 s.
A reaction path analysis of the catalytic partial oxidation of methane by transient experiments

![Graph showing selectivities to CO and H₂ as a function of time interval between oxygen and methane pulse.](image)

**Figure 7.4**: Selectivities to CO and H₂ as a function of the time interval between the oxygen and methane pulse. Alternating pulse experiment starting with oxygen at 973 K over rhodium sponge (2.1 wt. % Rh₂O₃) and a methane to oxygen feed molar ratio of 0.5.

Next, an experiment starting with methane was performed, the time interval being varied between zero and 1.0 s. The selectivity to CO increases from 7 % when simultaneous pulsing to 46 % at a time interval of 0.5 s, while the corresponding selectivity to H₂ increases from 18 % to 70 %. Increasing the time interval further to 1 s has no influence on the selectivities to CO and H₂. From a time interval of 0.5 s onwards the oxygen was introduced into the reactor when no gaseous methane was present anymore in the catalyst bed. No formation of carbon containing reaction products was observed during the interaction of oxygen with the catalyst. The normalised responses of CO, H₂, CO₂ and H₂O applying a time interval of 0.1 s between the methane and oxygen pulse are shown in Figure 7.5. The starting point and peak maximum of CO are observed prior to those of CO₂. A similar conclusion can be drawn from the responses of H₂ and H₂O. Furthermore, as soon as oxygen is introduced into the reactor and thus chemisorbed oxygen species are formed, the formation of CO₂ abruptly increases, while that of CO decreases. Similar behaviour of the H₂ and H₂O responses is observed, though the effects are less pronounced due to the fact that most gaseous hydrogen has already left the reactor at the moment dioxygen is introduced. At smaller time intervals between the methane and oxygen pulse the decrease in the hydrogen response is much more pronounced.
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Figure 7.5: Normalised responses of CO (x 2.4), CO₂ (x 1.7), H₂ and H₂O (x 4.3) as a function of time. Alternating pulse experiment starting with methane followed by oxygen at a time interval of 0.1 s. Rhodium sponge (2.1 wt. % Rh₂O₃), a methane to oxygen feed molar feed ratio of 0.5 and a temperature of 973 K.

7.4.4 Simultaneous interaction of methane and oxygen with rhodium during pulse experiments

The simultaneous interaction of methane and oxygen with the catalyst was investigated applying both unlabelled and labelled dioxygen. No oxygen was detected quantitatively and the carbon, hydrogen as well as oxygen balances were always closed. The role of oxygen present as Rh₂O₃ versus adsorbed oxygen in the partial oxidation of methane was investigated by a multipulse experiment of CH₄ and ¹⁸O₂ at a stoichiometric feed ratio. Prior to the experiment the catalyst was treated with a steady flow of CH₄ and ¹⁶O₂ at a stoichiometric feed ratio, which means that Rh₂¹⁶O₃ is present. Eight pulses of CH₄ and ¹⁸O₂ were introduced into the reactor with a 5 s time interval between the pulses. Formation of H₂ (S = 95%), H₂¹⁶O (S = 2.6 %), H₂¹⁸O (S = 2.4 %), C¹⁶O₂ (S = 2.9 %) and C¹⁶O¹⁸O (S = 1.1 %) was observed already during the first pulse and the selectivities remained the same during the subsequent seven pulses of the multipulse experiment. The selectivities to C¹⁶O and C¹⁸O as a function of the pulse number are shown in Figure 7.6, which is a compilation of the results of two multipulse experiments. In between the two experiments the state of the catalyst was restored by treatment with a steady flow of CH₄ and ¹⁶O₂ at a stoichiometric feed ratio until no formation of labelled products was observed any more. During the
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first pulse no formation of C\textsuperscript{18}O was observed, see Figure 7.6, and the selectivity increases up to 25 % at the eighth pulse. The selectivity to C\textsuperscript{16}O decreases from 96 % to 71 %, which means that the cumulative selectivity to CO remains constant at a level of 96 % during the multipulse experiment. During the first pulse 95 % of the \textsuperscript{18}O was incorporated into the catalyst, which decreases to 70 % at the eighth pulse.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure7_6.png}
\caption{Selectivities to C\textsuperscript{16}O and C\textsuperscript{18}O as a function of the pulse number. Multipulse experiment of eight pulses of CH\textsubscript{4}/\textsuperscript{18}O\textsubscript{2} at a feed molar ratio of 2 at 973 K over rhodium sponge (0.4 wt. % Rh\textsubscript{2}\textsuperscript{16}O\textsubscript{3}).}
\end{figure}

Simultaneous pulse experiments of CH\textsubscript{4} and \textsuperscript{16}O\textsubscript{2} were carried out at 923 K, 973 K and 1023 K at feed molar ratios of 2, 1 and 0.5. Prior to the experiments the catalyst was treated with a steady flow of CH\textsubscript{4} and O\textsubscript{2} in the same molar ratio as the experiment to follow. The selectivities to CO and H\textsubscript{2} at 973 K increase from 7 % and 18 % at a ratio of 0.5, to 34 % and 64 % at a ratio of 1 and finally to 90 % and 94 % at a ratio of 2. The selectivities to CO and H\textsubscript{2} are hardly influenced by the reaction temperature in the range of 923 K to 1023 K.

The normalised responses of CO, CO\textsubscript{2}, H\textsubscript{2} and H\textsubscript{2}O from a simultaneous pulse experiment of CH\textsubscript{4} and \textsuperscript{16}O\textsubscript{2} at a stoichiometric feed ratio at 973 K are shown in Figure 7.7. The starting point and maximum of the H\textsubscript{2} response are observed before those of the H\textsubscript{2}O response. Furthermore, the starting point and maximum of the CO response are observed before those of the CO\textsubscript{2} response.
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7.4.5 Simultaneous interaction of methane and oxygen with rhodium during steady flow experiments

Experiments with a steady flow of methane and oxygen with feed molar ratios of 2, 1 and 0.5 were carried out to investigate the influence of reaction temperature and feed molar ratio on the conversion and product selectivities. In none of the experiments dioxygen was detected quantitatively nor were \( \text{C}_2 \) products observed. The carbon, hydrogen as well as oxygen balances were closed. The conversion of methane and selectivities to \( \text{CO} \) and \( \text{H}_2 \) are shown in Figure 7.8 and 7.9 for a \( \text{CH}_4 / \text{O}_2 \) feed molar ratio of 2. Figure 7.8 shows that the methane conversion increases from 30 % at 773 K to nearly complete at 973 K. The corresponding selectivities to \( \text{CO} \) and \( \text{H}_2 \) increase from 76 % and 29 % to 100 %, see Figure 7.9. At a feed molar feed ratio of 1, the conversion of methane increases from 44 % at 773 K to 100 % at 823 K. The selectivity to \( \text{H}_2 \) increases from 2 % at 773 K to 77 % at 823 K and then slightly decreases to 72 % at 1023 K, while the selectivity to \( \text{CO} \) increases from approximately zero up to 49 % in the same temperature range. In the case of a \( \text{CH}_4 / \text{O}_2 \) feed molar ratio of 0.5 the conversion of methane is nearly complete and solely \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) are produced in the temperature range of 773 K to 1023 K.
Figure 7.8: Conversion of methane as a function of temperature for rhodium (0.4 wt. % Rh$_2$O$_3$) and platinum sponge (0.9 wt. % PtO$_2$). Steady flow experiment of CH$_4$/O$_2$ at a feed molar ratio of 2. The oxygen conversion was complete in all experiments.

Figure 7.9: Selectivity to CO and H$_2$ as a function of temperature for rhodium (0.4 wt. % Rh$_2$O$_3$) and platinum sponge (0.9 wt. % PtO$_2$). Steady flow experiment of CH$_4$/O$_2$ at a feed molar ratio of 2. The oxygen conversion was complete in all experiments.
The amount of Rh$_2$O$_3$ present during the simultaneous interaction of methane and oxygen was investigated as a function of the methane to oxygen feed molar ratio at 973 K. As soon as the steady-state was reached, the flow of reactants was switched off and the amount of Rh$_2$O$_3$ was determined by means of H$_2$ multipulse reduction. The percentages of rhodium oxidised, assuming an oxide stoichiometry of Rh$_2$O$_3$, are shown in Table 7.2, for the three different CH$_4$ to O$_2$ feed molar ratios. The amount of Rh$_2$O$_3$ present at reaction conditions increases from 0.4 wt. % at a stoichiometric feed ratio to 2.1 wt. % at a methane to oxygen feed molar ratio of 0.5 at a temperature of 973 K. The first amounts to ten theoretical monolayers of atomic oxygen.

Table 7.2: Weight percentages of metal oxide present during the simultaneous interaction of methane and oxygen with rhodium at 973 K and platinum at 1023 K, as a function of the methane to oxygen feed molar ratio, assuming an oxide stoichiometry of Rh$_2$O$_3$ and PtO$_2$.

<table>
<thead>
<tr>
<th>CH$_4$/O$_2$ feed molar ratio</th>
<th>wt. % Rh$_2$O$_3$</th>
<th>wt. % PtO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>2.1</td>
<td>2.9</td>
</tr>
<tr>
<td>1</td>
<td>0.6</td>
<td>1.5</td>
</tr>
<tr>
<td>2</td>
<td>0.4</td>
<td>0.9</td>
</tr>
</tbody>
</table>

7.4.6 Simultaneous interaction of methane and oxygen with platinum during steady flow experiments

As for rhodium, experiments with a steady flow of methane and oxygen with feed molar ratios of 2, 1 and 0.5 were carried out. The total flow rate and the amount of surface metal atoms are equal to that in the case of rhodium. Dioxygen was not detected quantitatively in any of the experiments nor were C$_2$ products observed. The carbon, hydrogen and oxygen balances were always closed.

The results at a stoichiometric feed ratio are compared to that of rhodium in Figure 7.8 and 7.9. The conversion of methane, see Figure 7.8, is always higher for rhodium compared to platinum in the temperature range of 800 K up to 1000 K. The selectivities to H$_2$ and CO, see Figure 7.9, are also higher for rhodium compared to platinum. At 773 K the difference in H$_2$ selectivity amounts to 22 %, while that to CO amounts to 16 %. At 923 K the difference in methane conversion between rhodium and platinum amounts to 15 % and in the CO and H$_2$ selectivity 25 % and 7 %. At 1000 K the selectivities to CO and H$_2$ are comparable.
At a feed molar ratio of 1 the conversion of methane increases from 75 % at 773 K to 100 % at 973 K. The selectivity to CO increases from 15 % to 53 % in the temperature range of 773 K to 1023 K, while the corresponding selectivity to H₂ increases from 58 % to 71 %. At a feed molar ratio of 0.5 a complete conversion of methane to CO₂ and H₂O was observed in the temperature range of 773 K to 1023 K.

The amount of platinum oxide, assuming a stoichiometry of PtO₂, was determined as function of the feed molar ratio at a temperature of 1023 K. The results are presented in Table 7.2. The amount of PtO₂ present at reaction conditions increases with decreasing methane to oxygen molar ratio from 0.9 wt. % at a stoichiometric feed ratio to 2.9 wt. % at a feed molar ratio of 0.5 at a temperature of 1023 K. The first amounts to 48 theoretical monolayers of atomic oxygen.

7.5 Discussion

7.5.1 Interaction of dioxygen and methane with reduced rhodium

Exposure of the reduced rhodium catalyst to a steady flow of oxygen at 1073 K leads to the almost complete oxidation of the latter to Rh₂O₃. The incorporation of oxygen during the multipulse experiments, Figure 7.2, is attributed to the decomposition of the Rh₂O₃ phase at a pressure of 10⁻⁵ Pa and temperatures in the range of 875 K to 948 K. Contrary to platinum, dissolved oxygen species are not present since no constant value is reached in the amount of incorporated oxygen as a function of time maintaining the oxidised catalyst at 10⁻⁵ Pa. Moreover, by interaction of dioxygen rhodium is almost completely oxidised whereas platinum only to an extent equivalent to 6 wt. % PtO₂. The decomposition rate of Rh₂O₃ is relatively slow since at a temperature of 948 K only an amount of oxygen equivalent to five theoretical monolayers is removed from the catalyst after a period of 900 s. The time scale of a typical TAP experiment amounts to two seconds and therefore the decomposition of Rh₂O₃ can be neglected during the simultaneous pulse experiments of methane and oxygen.

The shift of the peak maximum of the individual oxygen responses to a larger time value than that of the argon response, see Figure 7.3, is attributed to the reversible adsorption of oxygen at the catalyst surface. These species are assigned as dissociatively chemisorbed oxygen species, formed by the interaction of dioxygen with the catalyst surface. The time scale for desorption of the chemisorbed oxygen species amounts to two seconds.
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The interaction of methane with reduced rhodium results in the formation of carbon adatoms and gaseous hydrogen. The apparent activation energy for methane decomposition of 15 kJ mol$^{-1}$ is in reasonable agreement with the value of 21 kJ mol$^{-1}$ reported by Brass and Ehrlich (1987) for the dissociative chemisorption of methane on rhodium films.

7.5.2 Steady-state of rhodium at temperatures and a gas composition typical for catalytic partial oxidation

Whereas the catalyst is almost completely oxidised to Rh$_2$O$_3$ in the presence of dioxygen alone, it is largely reduced during the simultaneous interaction of methane and oxygen at a stoichiometric feed ratio. The latter state corresponds to a steady-state as indicated by the closed balances. Only 0.4 wt. % Rh$_2$O$_3$ is present, equivalent to ten theoretical monolayers of atomic oxygen. At decreasing methane to oxygen feed molar ratio, the percentage of Rh$_2$O$_3$ present increases. During the simultaneous interaction of methane and oxygen both reduced rhodium and Rh$_2$O$_3$ must be present for the formation of synthesis gas. On a completely reduced catalyst only formation of surface carbon and hydrogen occurs whereas on a completely oxidised catalyst methane is not activated (Hofstadt, 1996).

A physical picture of a rhodium surface consisting of a matrix of metallic rhodium and islands of an oxide phase seems in line with literature results. The existence of a mixed phase, consisting of metallic Rh and Rh$_2$O$_3$ is reported by Peuckert (1984) and is stable up to 800 K - 850 K. The mixed phase may be represented as Rh$_2$O$_3$ clusters dispersed in a rhodium metal matrix. Salanov and Savchenko (1993A, 1993B) conclude that the formation of an island consisting of a surface oxide phase occurs at a temperature of 500 K up to 700 K and thermal decomposition takes place at 750 K up to 900 K to yield dioxygen. Janssen et al. (1994) studied the initial process of the oxidation of rhodium with field emission microscopy (FEM) and report formation of an oxide species on rhodium. This oxide species decomposes and oxygen desorbs between 800 K and 1000 K. The oxidative process is reported to be surface-structure sensitive: the more open and rough the surface area, the more easily the oxidation.

It seems likely a gradient exists of the rhodium oxide percentage as a function of the axial position in the catalyst bed due to the strong interaction of oxygen with rhodium at high temperatures. Indeed, simulation of a single oxygen pulse involving Knudsen diffusion, adsorption and desorption in a packed bed of rhodium showed that during the pulse the surface in the beginning of the catalyst bed was completely covered with oxygen whereas the surface at the end of the bed was not covered with oxygen at all. However, the existence of an axial
gradient in the rhodium oxide percentage has no implications for the proposed mechanism, as confirmed by pulse experiments of CO, H₂ and CO₂ at 1023 K over rhodium containing 0.4 wt. % Rh₂O₃. CO and H₂ were converted to CO₂ and H₂O, respectively, and CO₂ did not react at all, i.e. secondary reactions of CO₂, such as the dissociation to CO and oxygen adatoms, does not occur under these conditions.

7.5.3 Interaction of methane with chemisorbed oxygen on rhodium

The levelling off of the increasing selectivities to CO and H₂ from time intervals of two seconds between the pulsing of oxygen and methane onwards, see Figure 7.4, indicates that chemisorbed oxygen is involved in the non-selective reaction paths of the partial oxidation of methane. Figure 7.5 shows that as soon as chemisorbed oxygen species are formed, the formation of CO₂ from CO increases. In the case of H₂ and H₂O a similar behaviour is observed. These results indicate that chemisorbed oxygen species are involved in the consecutive oxidation of CO to CO₂ and H₂ to H₂O.

The absence of any carbon containing product formation during an alternating pulse experiment starting with methane for time intervals longer than 0.5 s indicates that reactive carbon species with a long life time are not present on the surface as long as oxygen species are present.

7.5.4 Primary product formation on rhodium

During the simultaneous interaction of methane and oxygen at a stoichiometric feed ratio, see Figure 7.7, the starting point and maximum of the H₂ response is observed prior to those of the response of H₂O. Similarly, the starting point and maximum of the CO response are observed prior to those of CO₂.

The order of appearance of H₂ and CO as well as H₂O and CO₂ as shown in Figure 7.7 indicates that the former products are formed prior to the latter. One could argue that the order of appearance is determined by differences in Knudsen diffusion and adsorption/desorption coefficients. The order of appearance obtained by simulating the above phenomena for CO, H₂, H₂O and CO₂, see Figure 7.1, corresponds to the order of appearance expected for a pulse experiment with CH₄ and O₂ with all four the reaction products formed in a parallel way. The starting point and maximum of CO₂ is observed prior to that of CO. It follows from Figure 7.7, that on the contrary during the simultaneous interaction of methane and oxygen the starting point and peak maximum of the CO response is observed prior to that of CO₂. It is concluded that CO is a primary reaction product. A similar conclusion is drawn for H₂ and H₂O, with hydrogen being the primary product.
During the simultaneous interaction of methane and oxygen at a stoichiometric feed ratio and closed balances, the direct formation of synthesis gas occurs. CO and H₂ are oxidised to CO₂ and H₂O via consecutive reaction paths.

7.5.5 Reaction mechanism on rhodium

The multipulse experiments of CH₄ and ^18O₂ provide detailed information on the role of oxygen present as Rh₂O₃ versus chemisorbed oxygen in the partial oxidation of methane. During the first pulse, no formation of C¹⁸O was observed while C¹⁶O is being formed, see Figure 7.6, which means that formation of CO only proceeds via oxygen present as Rh₂¹⁶O₃. The formation of C¹⁶O¹⁸O and C¹⁶O₂ during the first pulse indicates that both chemisorbed oxygen and Rh₂¹⁶O₃ are involved in the consecutive oxidation of C¹⁶O. Both chemisorbed oxygen and Rh₂¹⁶O₃ are involved in the consecutive oxidation of H₂ as well, since formation of H₂¹⁶O as well as H₂¹⁸O is observed during the first pulse. The role of chemisorbed oxygen in the consecutive oxidation of CO and H₂ was already concluded from the alternating pulse experiments and is in line with the labelled oxygen experiment.

Only 5 % of the total amount of ^18O pulsed in the first pulse, is incorporated into the reaction products. The remainder of the ^18O is incorporated into the catalyst, which results in the formation of labelled rhodium oxide. As a result, the selectivity to C¹⁶O decreases and that to C¹⁸O increases at increasing pulse number, see Figure 7.6.

Based on the experimental findings, the following reaction mechanism is proposed for the partial oxidation of methane over rhodium. Methane dissociates to carbon and hydrogen adatoms on reduced rhodium. It is assumed that the abstraction of H adatoms from CHₓ species by oxygen adatoms does not occur to a significant extent. This reaction would lead to the formation of OH species and finally to H₂O formation. However, the high selectivities to H₂ indicate that this is not a dominant reaction step. Oh et al. (1991) proposed a mechanism for methane oxidation over alumina supported noble metal catalysts in which oxygen adatoms react with a CHₓ species to form formaldehyde, which decomposes into CO and two hydrogen adatoms. The methane to oxygen feed molar ratio was varied between 0.2 and 1, and they report that the metal surface is predominantly covered with oxygen. This mechanism could account for primary formation of CO and H₂. However, no formation of formaldehyde was observed in the present study and the methane to oxygen feed molar ratio amounts to two, resulting in a much lower oxygen coverage during the experiments.
The direct formation of CO from methane is believed to occur via a reaction between carbon adatoms and oxygen present as rhodium oxide. Hydrogen is formed as primary reaction product as well, via the associative desorption of two hydrogen adatoms from reduced rhodium. The consecutive oxidation of CO and H₂ occurs both via oxygen present as rhodium oxide and via chemisorbed oxygen.

Buyevskaya et al. (1994) studied the partial oxidation of methane over 1 wt. % Rh/γ-Al₂O₃. It is concluded that CO is a secondary product, formed by a surface reaction between carbon deposits and CO₂, which are the primary products. However, their response analysis is complicated due to the high specific surface area of their catalyst, 91 m² g⁻¹ BET, which will influence the shape of the responses due to diffusion in the pores of the catalyst. In-situ DRIFTS studies performed on the same catalyst (Walter et al., 1994) led the authors to the conclusion that OH surface groups on the support are involved in the CHₓ conversion to CO via a reforming reaction. Apparently, different results are obtained from experiments performed on a supported rhodium catalyst compared to the rhodium sponge of the present study. It is suggested that the γ-Al₂O₃ support is not inert at reaction conditions, but can especially catalyse the total oxidation reactions.

The observations of the present study are consistent with the following mechanism for the formation of synthesis gas over rhodium:

\[ \sigma \]

\[
(1) \quad CH₄ + 5 * \rightarrow C * + 4 H * \\
(2) \quad C * + Rh_xO \rightarrow Rh_x^o * + CO + * \\
(3) \quad O_2 + 2 Rh_x^o \rightarrow 2 Rh_xO \\
(4) \quad 2 H * \rightarrow H_2 + 2 * + 2 \]

\[
2 CH₄ + O_2 \rightarrow 2 CO + 4 H_2
\]

where \( \sigma \) is the stoichiometric number.
The dissociation of methane, see reaction 1, and the formation of H\textsubscript{2}, see reaction 4, is believed to occur on reduced rhodium sites. The formation of CO proceeds via a redox cycle postulated by Mars and van Krevelen (1954) for selective oxidation reactions. The oxidation of the carbon adatoms to CO, see reaction 2, is accompanied by the reduction of rhodium oxide, which is reoxidised by incorporation of dioxygen into the catalyst, see reaction 3.

7.5.6 Comparison between rhodium and platinum

The partial oxidation of methane to synthesis gas over platinum has been reported upon previously (Mallens, et al., 1995) and is summarised below. On reduced platinum the decomposition of methane results in the formation of carbon and hydrogen adatoms. In the presence of dioxygen only, oxygen is present in three different forms: platinum oxide, dissolved oxygen and chemisorbed oxygen species. CO and H\textsubscript{2} are produced directly from methane via oxygen present as platinum oxide. Activation of methane involving dissolved oxygen provides a parallel route to CO\textsubscript{2} and H\textsubscript{2}O. Both platinum oxide and chemisorbed oxygen species are involved in the consecutive oxidation of CO and H\textsubscript{2}. In the presence of both methane and dioxygen at a stoichiometric feed ratio dissolved oxygen species are not present and hence, the dominant pathways are the direct formation of CO and H\textsubscript{2} followed by their consecutive oxidation. A Mars-van Krevelen redox cycle was postulated for the partial oxidation of methane over platinum.

The results of the steady flow experiments of CH\textsubscript{4} and O\textsubscript{2} at a stoichiometric feed ratio, see Figures 7.8 and 7.9, show that rhodium is a more active and selective catalyst than platinum at a comparable temperature. In the investigated temperature range the difference in the selectivity to CO is more pronounced than the difference in selectivity to H\textsubscript{2}.

Hickman and Schmidt (1993A) also observed a higher methane conversion over rhodium compared to platinum. Lapsewicz and Jiang (1992) reported that methane activation is the rate-limiting step in the partial oxidation of methane. The difference in methane conversion can then be explained by the observed difference in apparent activation energy for methane activation on platinum, 52 kJ mol\textsuperscript{-1} (Mallens et al., 1995), and rhodium, 15 kJ mol\textsuperscript{-1}.

Lapsewicz and Jiang (1992) explain observed differences in CO selectivity to the differences in ratios of surface species, such as oxygen, carbon and hydrogen adatoms. Since the chemisorption of oxygen is not activated, the ability of the catalyst to activate methane determines the ratios of surface species. At increasing carbon to oxygen adatom ratio, the CO formation will be favoured compared to the formation of CO\textsubscript{2} and a high hydrogen to oxygen adatom ratio is
beneficial for the hydrogen selectivity. Hence, the differences in the selectivity to CO as well as H\textsubscript{2} observed in the present study can also be explained from the viewpoint that rhodium has a much lower activation energy than platinum has for methane activation.

Contrary to the results of the present study, Hickman and Schmidt (1993A) observed comparable selectivities to CO on Pt and Rh applying an autothermally operated reactor. The optimal selectivities are S\textsubscript{H\textsubscript{2}} = 43 % and S\textsubscript{CO} = 89 % for the platinum catalyst compared to S\textsubscript{H\textsubscript{2}} = 73 % and S\textsubscript{CO} = 90 % for the rhodium catalyst. The difference in the H\textsubscript{2} selectivity was explained by the higher activation energy for OH formation on Rh, 84 kJ mol\textsuperscript{-1}, compared to platinum, 11 kJ mol\textsuperscript{-1}. Therefore, on rhodium hydrogen adatoms are more likely to combine and desorb as H\textsubscript{2} than on Pt, which allows a faster formation of OH species. This reasoning may also provide an explanation for the higher H\textsubscript{2} selectivity of rhodium observed in the present study, in addition to the difference in the activation energy of methane activation. The discrepancy concerning the CO selectivities between the present study and the observations of Hickman and Schmidt (1993A) can be explained by the difference in reaction mechanism. The balance between the rate of the oxidation and reduction steps determines the amount of metal oxide present at steady-state. The lower amount of rhodium oxide present at steady-state compared to platinum oxide at a stoichiometric feed ratio may explain the higher CO selectivity on rhodium since this could also correspond to a lower rate of the consecutive oxidation reaction of CO.

By interaction with dioxygen, rhodium is almost completely oxidised to Rh\textsubscript{2}O\textsubscript{3} at 1073 K and the formation of this oxide phase was confirmed by ex-situ XRD and XPS measurements. For platinum a maximum amount of oxide equivalent to 6 wt. % PtO\textsubscript{2} was formed at 1023 K. However, the presence of a PtO\textsubscript{2} phase could not be confirmed by an ex-situ XRD analysis. Dissolved oxygen species were not observed in the case of rhodium during the interaction with dioxygen, probably due to the almost complete oxidation of rhodium to Rh\textsubscript{2}O\textsubscript{3}.

During the simultaneous interaction of methane and oxygen the percentage of metal oxidised is larger for platinum than for rhodium, see Table 7.2. The difference is most pronounced at a stoichiometric feed ratio. In the steady-state the amount of metal oxide results from the rate of metal oxidation by oxygen and the rate of oxide reduction by carbon adatoms. Hence, the differences between platinum and rhodium as shown in Table 7.2 may be explained by the lower activation energy for methane decomposition on rhodium, resulting in a higher concentration of carbon adatoms and thus a higher rate of oxide reduction.
7.6 Conclusions

During the interaction of dioxygen with rhodium sponge, the catalyst is almost completely oxidised to Rh$_2$O$_3$. Besides rhodium oxide, oxygen is also present in the form of chemisorbed oxygen species. During the simultaneous interaction of methane and dioxygen at a stoichiometric feed ratio and a temperature of 973 K the catalyst is mainly in the metallic rhodium phase.

The decomposition of methane on reduced rhodium results in the formation of carbon and hydrogen adatoms. Synthesis gas is a primary product. Hydrogen is formed via the associative desorption of two hydrogen adatoms from reduced rhodium and the reaction between carbon adatoms and oxygen present as rhodium oxide results in the formation of carbon monoxide. The consecutive oxidation of CO and H$_2$ proceeds via both chemisorbed oxygen and oxygen present as rhodium oxide. A Mars-van Krevelen mechanism is postulated for the partial oxidation of methane over rhodium: methane reduces the rhodium oxide, which is reoxidised by dioxygen.

When compared to platinum, rhodium shows a higher methane conversion at a comparable temperature and also a higher selectivity to both CO and H$_2$. All differences can be explained by the activation energy for methane decomposition which is higher on platinum than on rhodium. An additional explanation for the observed difference in the H$_2$ selectivity could be the higher activation energy for OH formation on rhodium compared to platinum.

References


A reaction path analysis of the catalytic partial oxidation of methane by transient experiments


Hofstadt, K., Personal Communication, 1996.


The reaction mechanism of the partial oxidation of methane to synthesis gas: a transient kinetic study over rhodium and a comparison with platinum


Appendix 7A: Parameter values used in the simulations

Parameter values used in the simulation for the reaction A + * → A* at 973 K, by solving continuity equations 7.9 and 7.10 with initial and boundary conditions 7.11-7.14.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{e,H_2}^K$ (inert bed)</td>
<td>$1.5 \times 10^{-2} \text{ m}^3 \text{ m}^{-1} \text{s}^{-1}$</td>
</tr>
<tr>
<td>$D_{e,H_2}^K$ (catalyst bed)</td>
<td>$2.3 \times 10^{-2} \text{ m}^3 \text{ m}^{-1} \text{s}^{-1}$</td>
</tr>
<tr>
<td>$D_{e,H_2O}^K$ (inert bed)</td>
<td>$5.4 \times 10^{-3} \text{ m}^3 \text{ m}^{-1} \text{s}^{-1}$</td>
</tr>
<tr>
<td>$D_{e,H_2O}^K$ (catalyst bed)</td>
<td>$8.1 \times 10^{-3} \text{ m}^3 \text{ m}^{-1} \text{s}^{-1}$</td>
</tr>
<tr>
<td>$D_{e,CO}^K$ (inert bed)</td>
<td>$4.3 \times 10^{-3} \text{ m}^3 \text{ m}^{-1} \text{s}^{-1}$</td>
</tr>
<tr>
<td>$D_{e,CO}^K$ (catalyst bed)</td>
<td>$6.5 \times 10^{-3} \text{ m}^3 \text{ m}^{-1} \text{s}^{-1}$</td>
</tr>
<tr>
<td>$D_{e,CO_2}^K$ (inert bed)</td>
<td>$3.4 \times 10^{-3} \text{ m}^3 \text{ m}^{-1} \text{s}^{-1}$</td>
</tr>
<tr>
<td>$D_{e,CO_2}^K$ (catalyst bed)</td>
<td>$5.2 \times 10^{-3} \text{ m}^3 \text{ m}^{-1} \text{s}^{-1}$</td>
</tr>
<tr>
<td>$\epsilon_b$ (inert bed)</td>
<td>$0.5 \text{ m}^3 \text{ m}^{-3}$</td>
</tr>
<tr>
<td>$\epsilon_b$ (catalyst bed)</td>
<td>$0.6 \text{ m}^3 \text{ m}^{-3}$</td>
</tr>
<tr>
<td>$d_p$ (inert bed)</td>
<td>$2.5 \times 10^{-4} \text{ m}$</td>
</tr>
<tr>
<td>$d_p$ (catalyst bed)</td>
<td>$3.0 \times 10^{-4} \text{ m}$</td>
</tr>
<tr>
<td>$r_b$</td>
<td>$5.6 \text{ m}^2 \text{ m}^{-2}$</td>
</tr>
<tr>
<td>$a_v$</td>
<td>$8.9 \times 10^5 \text{ m}<em>{\text{cat}}^2 \text{ m}</em>{\text{cat}}^{-3}$</td>
</tr>
<tr>
<td>$N_p$</td>
<td>$2.2 \times 10^{-5} \text{ mol}$</td>
</tr>
<tr>
<td>$l_1$</td>
<td>$1 \times 10^{-2} \text{ m}$</td>
</tr>
<tr>
<td>$l_2$</td>
<td>$5.10^{-3} \text{ m}$</td>
</tr>
<tr>
<td>$l_3$</td>
<td>$1 \times 10^{-2} \text{ m}$</td>
</tr>
<tr>
<td>$k_{\text{ads, H}_2}$</td>
<td>$1.38 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{s}^{-1}$</td>
</tr>
<tr>
<td>$k_{\text{des, H}_2}$</td>
<td>$4.59 \times 10^8 \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$k_{\text{ads, H}_2O}$</td>
<td>$4.53 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{s}^{-1}$</td>
</tr>
<tr>
<td>$k_{\text{des, H}_2O}$</td>
<td>$3.77 \times 10^{10} \text{ s}^{-1}$</td>
</tr>
<tr>
<td>$k_{\text{ads, CO}}$</td>
<td>$1.17 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{s}^{-1}$</td>
</tr>
<tr>
<td>$k_{\text{des, CO}}$</td>
<td>$3.27 \times 10^6 \text{ s}^{-1}$</td>
</tr>
</tbody>
</table>
GENERAL CONCLUSIONS

The catalytic conversion of methane to ethene or synthesis gas in the presence of dioxygen was investigated applying a Temporal Analysis of Products set-up. Sampling of the product stream from a few milliseconds on with a submillisecond time resolution allowed to investigate the interaction of methane and oxygen with the surface at an initial stage of reaction, leading to detailed information on the reaction network of these processes. The small amount of molecules per pulse ensures that gas phase reactions can be neglected, i.e. solely the heterogeneous reactions are studied at a well defined state of the catalyst surface. Unique information on the life time and reactivity of adsorbed species could be obtained at the high temperatures involved. Titration experiments allowed to study the total amount of oxidic oxygen in relation to the catalyst composition or reaction conditions.

Equilibrium calculations were carried out to obtain insight into the thermodynamic stability of the possible species in the system oxygen/methane, oxygen platinum and oxygen/rhodium. At a methane to oxygen feed molar ratio of 0.5 the gas mixture at equilibrium solely consists of carbon dioxide and water at temperatures varying from 300 K to 1500 K. At ratios of 1, 2 and 3 the components methane, carbon dioxide, water and solid elementary carbon are present at low temperatures. At increasing temperature also carbon monoxide and hydrogen are present at equilibrium. The composition at high temperatures depends on the methane to oxygen feed molar ratio. At a ratio of 1 hydrogen, carbon monoxide, carbon dioxide and water are present, while at a ratio of 2 the gas mixture solely consists of hydrogen and carbon monoxide. Solid elementary carbon is also present at a ratio of 3 at high temperatures, besides hydrogen and carbon.
monoxide. Ethane and ethene were not present at equilibrium up to a methane to oxygen feed molar ratio of 3. Equilibrium calculations on the systems oxygen/platinum and oxygen/rhodium led to the conclusion that platinum oxide in the form of PtO₂ is stable at much higher oxygen partial pressures compared to rhodium oxide, in the form of Rh₂O₃.

The oxidative coupling of methane has been studied in the presence of three catalysts based on magnesium oxide: MgO, Li/MgO and Sn/Li/MgO. The oxidative coupling of methane over Sn/Li/MgO in the presence of both methane and dioxygen at a temperature of 973 K proceeds as follows. Methyl radicals are produced at the surface and formation of ethane occurs in the gas phase via the coupling of two methyl radicals. Ethene is produced from ethane via a gas phase reaction in which dioxygen is involved. This reaction may involve surface produced ethyl radicals. Both ethane and ethene are oxidised to carbon monoxide at the surface. The oxidation of carbon monoxide to carbon dioxide proceeds via the surface. In parallel to the formation of ethane, methane is directly converted to carbon dioxide by a heterogeneous reaction.

Two types of reversibly adsorbed oxygen are present in the case of Sn/Li/MgO. The first type is strongly adsorbed oxygen, with a time scale for desorption amounting to three minutes at 973 K. This type of oxygen species is not active in the oxidative coupling reactions at all. The second type concerns weakly adsorbed oxygen species, which are completely desorbed after a time interval of four seconds at 973 K. This type of adsorbed oxygen species is involved in the direct conversion of methane to carbon dioxide.

Besides reversibly adsorbed oxygen also two types of surface lattice oxygen are present in the case of Li/MgO and Sn/Li/MgO. The first is active in the production of methyl radicals, while the second is active in the direct conversion of methane to carbon dioxide. Weakly adsorbed oxygen species and the second type of surface lattice oxygen are also active in the non-selective reaction paths of ethane and ethene as well as the consecutive oxidation of carbon monoxide.

The percentage of surface lattice oxygen which is active in the methane coupling reactions amounts to less than 0.1 % of a theoretical monolayer in the case of MgO at 1023 K. These values are 27 % for Li/MgO and 44 % for Sn/Li/MgO at the same temperature. The increase in the amount of active surface lattice oxygen as a result of the addition of lithium and moreover tin to magnesium oxide explains the increase in the activity of the catalysts in this order.

The partial oxidation of methane to synthesis gas has been investigated for platinum and rhodium sponge as catalyst. The interaction of pure dioxygen with reduced rhodium results in the complete oxidation to Rh₂O₃. Besides rhodium oxide
also chemisorbed oxygen species are present, with a time scale for desorption amounting to two seconds. In the case of platinum only a partial oxidation occurs to an amount equivalent to 6 wt. % PtO₂. Besides platinum oxide also chemisorbed oxygen species and dissolved oxygen species are present. The dissolved oxygen species are completely desorbed after five minutes and the time scale for desorption of the chemisorbed oxygen species amounts to two seconds. The metal oxides are stable on an hour time scale. During the simultaneous interaction of methane and oxygen at a stoichiometric feed ratio for the production of synthesis gas the amount of platinum and rhodium oxide present is less than 1 wt. %. The reaction occurs via a Mars-van Krevelen mechanism: methane reduces the metal oxide, which is reoxidised by dioxygen from the gas phase.

Synthesis gas is produced as primary product. Methane dissociates to carbon and hydrogen adatoms on reduced surface sites. Hydrogen is produced via the associative desorption of hydrogen adatoms and the reaction between carbon adatoms and oxygen in de form of platinum or rhodium oxide results in the formation of carbon monoxide. The consecutive oxidation of hydrogen and carbon monoxide occurs via both chemisorbed oxygen species and oxygen in the form of an oxide. In the case of platinum methane is directly converted to carbon dioxide and water by involvement of dissolved oxygen species in parallel to the formation of synthesis gas.

Rhodium is a more active catalyst for the conversion of methane and also shows a higher selectivity to synthesis gas, the selectivity to carbon monoxide being the most pronounced. The differences are explained by the higher activation energy of methane dissociation on platinum compared to rhodium.
A reaction path analysis of the catalytic partial oxidation of methane by transient experiments
LIST OF PUBLICATIONS

The following papers related to the work presented in this thesis have been published or will be published:


A reaction path analysis of the catalytic partial oxidation of methane by transient experiments
Gedurende mijn promotieonderzoek hebben verschillende mensen een bijdrage geleverd aan de resultaten beschreven in dit proefschrift of technische ondersteuning verleend voor het draaiende houden van de experimentele opstelling. Graag wil ik iedereen hiervoor van harte bedanken. Tot diegenen waarmee ik het meest intensief heb samengewerkt, wil ik me kort persoonlijk richten.

Jeroen en Eric, als afstudeerders hebben jullie een belangrijke bijdrage geleverd aan de inhoud van dit proefschrift. Naast jullie inzet en initiatief denk ik terug aan een leerzame periode van mijn promotie, waarbij ik op een prettige manier met jullie heb samengewerkt.

Ton, met eindeloos veel geduld heb je diverse reparaties aan de opstelling verricht, waarbij Murphy’s law regelmatig op waarheid is getest. Nuttig was ons bezoek aan de RU Gent, om daar de fijne kneepjes van het TAP apparaat te leren.

Jozef, ik kon altijd bij je terecht met mijn vragen; jouw suggesties en opmerkingen zijn van groot belang geweest voor het onderzoek. Het enthousiasme dat je uitstraalde, heb ik als zeer positief ervaren.

Guy, met jouw enorme kennis wist je telkens de zwakke plekken in mijn betoog bloot te leggen. Je hebt me de vrijheid gegund mijn eigen weg te volgen en je stimulerende manier van begeleiden zijn voor mij zeer waardevol geweest. De deelname aan het symposium in Sydney was voor mij een ervaring waaruit ik veel energie heb geput gedurende de rest van mijn promotieonderzoek.

Tenslotte wil ik alle AIO’s, vaste medewerkers en afstudeerders van de groep bedanken. Jullie maakten het tot een periode waar ik met veel plezier aan terug denk. Hierbij wil ik even speciaal vermelden de, ik mag wel zeggen, legendarische LCT-dagen alsmede de fanatieke squashpartijen.
A reaction path analysis of the catalytic partial oxidation of methane by transient experiments
CURRICULUM VITAE

A reaction path analysis of the catalytic partial oxidation of methane by transient experiments
Stellingen

behorende bij het proefschrift

A Reaction Path Analysis of the Catalytic Partial Oxidation of Methane by Transient Experiments

van Erik Mallens

1. De toename in de aktiviteit van magnesiumoxide voor de omzetting van methaan door de toevoeging van lithium en bovenal tin kan verklaard worden door de toename in de hoeveelheid aktieve roosterzuurstofatomen. Hoofdstuk 5 van dit proefschrift.

2. Koolmonoxide en molekulair waterstof zijn de primaire reaktieprodukten in de katalytische partiële oxydatie van methaan door zuurstof over platina- en rhodiumkatalysatoren bij temperaturen in de orde grootte van 973 K. Hoofdstuk 7 van dit proefschrift.

3. De conclusie van Buyevskaya et al. dat het tweede maximum in het uitlaatsignaal van zuurstof, tijdens een alternerend pulseexperiment van zuurstof en methaan, duidt op aanwezigheid van molekulair geadsorbeerd zuurstof is onjuist.


4. Voor een betrouwbare bepaling van de reaktietemperatuur bij zeer exotherme heterogene gekatalyseerde reakties, is het noodzakelijk het gehele axiale temperatuurprofiel over het katalysatorbed te meten.


5. Het aantal deelnemers aan een wetenschappelijk symposium wordt niet alleen bepaald door het onderwerp, maar ook door de keuze van de plaats waar het georganiseerd wordt.

6. Het begrip "biologische landbouw", als aanduiding voor het telen van gewassen zonder gebruik van bestrijdingsmiddelen, is de moeder van alle pleonasmen.

7. De olympische gedachte "deelnemen is belangrijker dan winnen" is een achterhaald begrip.

8. Veel Nederlandse politici hebben een slecht ontwikkeld gevoel voor de maatschappelijke realiteit.

9. De economische drive om luchthaven Schiphol uit te laten groeien tot één van de mainports van Europa en het politieke besluit het aantal passagiers te laten stijgen tot maximaal 44 miljoen per jaar zijn niet verenigbaar.
Klein, T., de Volkskrant, 20 juli 1996.

10. Het ontbreken van een duidelijke relatie tussen de hoogte van de eindexamencijfers op het VWO en de kwaliteit van de afgestudeerden, maakt loting een rechtvaardig selektiemiddel voor het toelaten van studenten tot studierichtingen met een numerus fixus.

11. Het afschaffen van de opkomstplicht voor dienstplichtige militairen leidt tot grote sociale veranderingen in het leger.