Silicon-technology based microreactor design for high temperature heterogeneous reactions

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Silicon-technology based microreactor design for high temperature heterogeneous reactions

PROEFSCHRIFT

ter verkrijging van de graad van doctor aan de Technische Universiteit Eindhoven, op gezag van de Rector Magnificus, prof.dr.ir. C.J. van Duijn, voor een commissie aangewezen door het College voor Promoties in het openbaar te verdedigen op donderdag 15 februari 2007 om 16.00 uur

door

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Summary

Microreaction technology allows the fabrication of chemical reactors with sub-millimeter dimensions. The reduction in size as compared to conventional systems offers several advantages like improved heat and mass transfer. The focus of the work presented in this thesis, has been on a silicon based microchemical system for the catalytic partial oxidation (CPO) of methane. In this catalytic reaction, methane is converted to synthesis gas over a noble metal catalyst. Synthesis gas, a mixture of carbon monoxide and hydrogen, is one of the most important intermediates in the chemical industry. Moreover, methane conversion to synthesis gas can be used as a hydrogen source after removing carbon monoxide. Small scale hydrogen production can then be used for fuel cells for powering domestic or automotive applications.

In this thesis, the results of a feasibility study are given for silicon based microreactors with integrated heaters and temperature sensors for the catalytic partial oxidation of methane. The microreactors designed in this study are to be used for reaction kinetic research on this fast, high temperature, partial oxidation reaction. Making use of a microreactor for this purpose can have the advantage of improved heat and mass transport, suppression of gas phase reactions, and fast and accurate control of the reaction conditions resulting in more reliable reaction kinetic data.

Catalyst support materials were tested for their functionality, i.e. activity and stability under reaction conditions. Sputtered and spin coated rhodium catalysts were studied, by making use of different interlayers grown on top of flat silicon substrates (Si, Ta/SiO$_2$/Si, SiO$_2$/Si, Si$_3$N$_4$/Si, and SiRN/Si). Rhodium catalysts on these support substrates are used for hydrogen oxidation and catalytic partial oxidation (CPO) of methane. Hydrogen oxidation is executed as this catalytic oxidation reaction can be used at milder reaction conditions (470 K) compared to CPO (1000 - 1200 K). During both reactions, catalyst activ-
Summary

Activity was measured in time. For both reactions and for most substrates an initial high conversion was observed for 30 to 60 minutes on stream. However, after 1-2 hours on stream, no catalytic activity can be observed any more, for most of the substrates, and for both reactions. Catalytic partial oxidation of methane to synthesis gas was found to be best on Si platelets with a SiRN interlayer, with high conversion and selectivities measured: \( X_{O_2} = 97 \% \), \( X_{CH_4} = 57 \% \), \( S_{H_2} = 0.72 \), and \( S_{CO} = 0.80 \). ToF-SIMS experiments revealed that during both hydrogen oxidation and CPO reactions, the Rh catalyst becomes covered with silicon containing components by diffusion from the substrates. The silicon diffusion to the outer surface of the catalytic layer explains the catalyst deactivation during time on stream.

The microreactor had to fulfill a variety of constraints to be able to perform the catalytic partial oxidation reaction. Within these constraints a microreactor is designed, consisting of a square reaction channel, closed at the topside by a flat 1 \( \mu \)m thin wall. Heaters and temperature sensors are positioned on top of this thin wall, while the rhodium catalyst is deposited underneath it. Direct control of the catalytic reaction temperature is therefore possible. CPO of methane has a high conversion and selectivity to synthesis gas on a rhodium catalyst at catalyst temperatures of 1100 K. A detailed thermal analysis of the microreactor is made, and it was found by calculations that the reaction temperature of 1100 K can be reached at the catalyst with 1.5 W of heating power per heater while the rest of the reactor is maintained at a temperature of 350 K. The low temperature of the rest of the reactor is necessary to preserve the electrical connections and the gas seals. The reaction gases are preheated to the reaction temperature before they reach the catalyst positioned directly under the heaters of the reactor. The catalyst position is determined in such a way that the reaction will not reach full conversion to be able to observe reaction kinetics from the reaction selectivities.

Different generations of microreactors were built and tested, all with their own characteristics. The succeeding generations of microreactors are based on design issues, developments in the microreactor production process, and experimental experiences obtained. The thickness and thermal conductivity of the microreactor top wall is found crucial to reach the reaction temperature. Most of the heat released inside the channel top wall by the heaters and by the exother-
mic reaction is lost by conduction, 70-90%. The first microreactor prototypes consisted of a flat top wall containing a heavily boron-doped mono-crystalline silicon (p++Si) and a low stress silicon-rich nitride (SiRN) or silicon nitride (Si₃N₄) layer. Although the composite top wall of the microreactors are strong enough to withstand thermally induced stresses, the operation temperature of these reactors is limited due to electrical breakdown of the SiRN and Si₃N₄ layer. A microreactor with a top wall consisting of 850 nm p++Si and 150 nm SiRN can be operated up to a temperature of 580 K. Changing the SiRN layer for 200 nm Si₃N₄, which has a higher critical field strength, the temperature operating window is enlarged to 870 K. At these high temperatures, it was observed that the electrical properties of the heaters and temperature sensors change due to degradation. The high temperature degradation can be omitted by first using the reactor at a higher temperature than the temperature used in the experiments. Hydrogen oxidation was performed in the microreactor with the channel top wall consisting of 200 nm Si₃N₄ on top of 850 nm p++Si. Mixtures of hydrogen and oxygen were catalytically oxidized safely at temperatures between 560 - 670 K, proving the inherent safety of microreactors with flammable gas mixtures. Although deactivation was found on the catalyst substrate platelets, no deactivation was observed during operation of the microreactors.

The heat and mass transport was studied inside the micro channel by means of computational fluid dynamic (CFD) calculations, analytical model calculations, and by experiments. Empirical Nusselt and Sherwood correlations as a function of the Graetz number were derived. When the inlet gases are colder than the side and bottom wall of the channel, a heat flux reversal is observed on the side and bottom walls of the channel. When the inlet gas temperature is equal to the temperature of the side and bottom walls, the asymptotic value of the Nusselt number is the highest and the temperature development length the shortest. A high Nusselt number results in a high heat transfer coefficient which is preferred for kinetic research because hot-spot formation and run-away reactions can be prevented. A model was made for the mass transport limited CPO of methane in the square reaction channel. The model can be used to extract kinetic data from the reaction selectivity obtained by experiments. However, in the microreactors no CPO of methane could be performed and only modeling results are presented. When helium is used instead of nitrogen as inert gas in the reactor feed, the density of the gas mixture and therefore the Reynolds
number decrease. The lower Reynolds number results in a lower local Sherwood number. Despite the lower Sherwood number, the oxygen conversion increases with 14% as the diffusion coefficients of components are higher in helium compared to nitrogen. Thermal diffusion was taken into account in the modeling results because a temperature gradient of about $1.5 \cdot 10^6$ K/m exists between the top and bottom channel wall. It is found that thermal diffusion has almost no effect on the conversion and changes the species concentrations at the catalytic surface by 0.01% at most. The influence of thermal diffusion can therefore be neglected in the mass transport model, simplifying the model equations.

Microreactors with a flat channel top wall were found to have a limited operation temperature of 870 K due to electrical breakdown of silicon nitride in the channel top wall. For stable operation of the catalytic partial oxidation of methane, the operation temperature should be increased further. Because $p^{++}$ Si is electrically conducting, it should be omitted near the heater elements to prevent electrical breakdown. However, microreactors with channel top walls consisting of SiRN or Si$_3$N$_4$ only are more vulnerable to mechanical failure due to large thermally induced stresses. In a new reactor design, the heaters are deposited inside a suspended SiRN tube. The SiRN tubes provide a corrugated zone to release mechanical stress during heating. These suspended heater microreactors are stably operated for 110 hours at 900 K. At higher temperatures, the heaters started to degrade, leading to shorter live times. Within the projects time frame no suspended heater microreactors with catalyst could be made. Although no catalytic reaction could be performed, it is expected that this silicon microreactor can be stably operated at temperatures around 1100 K, i.e. at CPO reaction conditions, for several hours. Therefore it can be argued that by making use of a suspended heater reactor, the reaction kinetics of catalytic partial oxidation reaction of methane can be studied inside a silicon-based microreactor.
Samenvatting

Microreactortechnologie geeft de mogelijkheid om chemische reactoren te maken met submillimeter afmetingen. Deze gereduceerde afmetingen bieden deze reactoren verschillende voordelen boven conventionele reactoren, zoals een verbeterde warmte- en massaoverdracht. Het werk beschreven in dit proefschrift richt zich voornamelijk op een microreactorsysteem gebaseerd op silicium voor de katalytische partiële oxidatie (CPO) van methaan. Bij deze katalytische reactie wordt methaan omgezet in synthesegas met behulp van een edelmetaalkatalysator. Synthesegas, een mengsel van koolmonoxide en waterstofgas, is één van de belangrijkste tussenproducten in de chemische industrie. Methaanomzetting naar synthesegas kan ook gebruikt worden als een bron voor waterstofgasproductie, na het verwijderen van koolstofmonoxide. Het op kleine schaal produceren van waterstofgas kan dan gebruikt worden in brandstofcellen om elektriciteit op te wekken voor ondermeer het gebruik in huizen en voertuigen.

In dit proefschrift zijn de resultaten beschreven van een haalbaarheidsstudie naar het gebruik van een silicium microreactor met verwarmingselementen en temperatuursensoren voor de katalytische partiële oxidatie van methaan. Deze microreactor kan toegepast worden voor onderzoek naar de reactiekinetiek van deze snelle, bij hoge temperatuur uitgevoerde reactie. Het gebruik van een microreactor voor dit soort onderzoek kan verschillende voordelen opleveren, zoals een verbeterde warmte- en massaoverdracht, het onderdrukken van gasfasereacties en een snelle en precieze regeling van de reactiecondities. Deze voordelen kunnen dan uiteindelijk leiden tot een betrouwbaardere beschrijving van de kinetiek van deze reactie.

In een aanvullende studie zijn er katalysatoren op verschillende dragermaterialen getest voor hun functionaliteit d.w.z. hun activiteit en stabiliteit onder reactiecondities. Gesputterde en gespincoated rhodiumkatalysatoren op vlakke substraten als katalysatoronderlaag (Si, Ta/SiO₂/Si, SiO₂/Si, Si₃N₄/Si, SiRN/Si, en kwarts) zijn gebruikt. De rhodiumkatalysatoren op deze substraten zijn gebruikt voor waterstofoxidatie bij 470 K en voor CPO van methaan bij 1000-1200 K. Waterstofoxidatie is uitgevoerd omdat deze katalytische oxidatie reactie bij mildere reactiecondities (470 K) dan CPO (1000 - 1200 K) kan worden
Samenvatting

De hoge katalysatoractiviteit en selectiviteit van de katalytische partiële oxidatie van methaan bleken het beste uit te voeren op siliciumplaatjes met een SiRN tussenlaag met hoge gemeten conversies en selectiviteiten: \( X_{O_2} = 97\% \), \( X_{CH_4} = 57\% \), \( S_{H_2} = 0.72 \), and \( S_{CO} = 0.80 \). Uit ToF-SIMS experimenten is gebleken, dat zowel gedurende de waterstofoxidatie als tijdens de CPO-reactie de Rh-katalysator bedekt wordt met siliciumcomponenten. De siliciumdiffusie naar het oppervlakte van de katalysator verklaart de katalysatordeactivering gedurende de reactie.

De te ontwerpen microreactor moet voldoen aan verschillende voorwaarden om de katalytische partiële oxidatie van methaan uit te kunnen voeren. Een microreactor met een vierkant reactiekanaal, 1 µm dunne wand en een vlakke bovenzijde, en verwarmingselementen en temperatuursensoren aangebracht, terwijl aan de onderzijde een rhodiumkatalysator is afgezet. OP deze manier kan de temperatuur van de katalysator direct worden gemeten en geregeld. CPO van methaan heeft hoge conversie en selectiviteit bij een katalysatortemperatuur van 1100 K. Uit een gedetailleerde thermische analyse van de microreactor blijkt dat de reactietemperatuur van 1100 K bereikt kan worden met een elektrisch vermogen van ongeveer 1.5 W per verwarmingselement, terwijl de rest van de reactor op 350 K gehouden wordt. Deze lage temperatuur voor de rest van de reactor is nodig om elektrische aansluitingen en gasaansluitingen relatief eenvoudig uit te voeren, zonder dat deze thermisch aangetast worden. De reactiegassen worden eerst voorverwarmd met de verwarmingselementen voordat deze de katalysator bereiken. De positie van de katalysator in het kanaal is zo gekozen dat de reactie geen volledige conversie zal hebben en er hierdoor reactiekinetiek uit de reactie-selectiviteit bepaald kan worden.

Verschillende generaties microreactoren met hun karakteristieke eigenschappen zijn gemaakt en getest. De opeenvolgende reactoren zijn gebaseerd op ontwerpstandaarden, ontwikkelingen in het productieproces en experimentele ervaringen. De dikte en de thermische geleidbaarheid van de micro-
reactortopwand is cruciaal om de reactietemperatuur te kunnen bereiken. De meeste warmte die vrijkomt in de bovenwand van de reactor door de verwarmingselementen en door de exotherme reactie gaat verloren door warmtegeleiding (70-90%). De eerste microreactorprototypes hadden een vlakke bovenwand opgebouwd uit zwaar boorgedoteerd monokristallijn silicium (p++Si) en een stress-arme siliciumrijke siliciumnitride (SiRN) of siliciumnitride (Si₃N₄) laag. Hoewel deze samengestelde reactorwanden opgewassen zijn tegen de thermische spanningen in het materiaal, was de bedrijfstemperatuur beperkt door elektrische doorslag van de SiRN en Si₃N₄ laag. Een microreactor met een bovenwand van 850 nm p++Si en 150 nm SiRN kon gebruikt worden tot een temperatuur van 580 K. Door het SiRN te vervangen door 200 nm Si₃N₄, dat een hogere kritische veldsterkte heeft, kon de bedrijfstemperatuur verhoogd worden tot 870 K. Bij deze hoge temperaturen werd waargenomen, dat de elektrische eigenschappen van de verwarmingselementen en de temperatuursensoren veranderden door degradatie. De hoge temperatuurdegradatie kan voorkomen worden door de reactor eerst te verwarmen tot een hogere temperatuur dan de temperatuur die gebruikt gaat worden in het experiment. In de reactor met een bovenwand van 200 nm Si₃N₄ en 850 nm p++Si is er waterstofoxideatie uitgevoerd. Mengsels van waterstof en zuurstof zijn veilig katalytisch geoxideerd bij temperaturen tussen de 560 en 670 K. Hiermee is het inherent veilig zijn van microreactoren met brandbare gasmengsels bevestigd. Hoewel er katalysatordeactivering was gevonden op de katalytische substraatplaatjes, werd er geen deactivering gevonden tijdens de experimenten met de microreactoren.

Het warmte- en massatransport in de microreactor is bestudeerd met behulp van computational fluid dynamic (CFD) berekeningen, analytische modelberekeningen en met experimenten. Empirische Nusselt- en Sherwood-correlaties zijn afgeleid als functie van het Graetz-getal. Als de gevoede gassen een lagere temperatuur hebben dan de zijwanden en bodemwand van het kanaal blijkt de warmteflux zich om te keren op deze wanden. Indien de gevoede gassen dezelfde temperatuur hebben als de zijwanden en bodemwand blijkt de asymptotische waarde van het Nusselt-getal maximaal en de lengte voor ontwikkeling van het temperatuursprofiel het kortst. Een hoog Nusselt-getal resulteert in een hoge massatransportcoëfficiënt welke wenselijk is voor kinetisch onderzoek, omdat hot-spots en run-away-reacties kunnen worden vermeden. Een
model is ontworpen voor massatransport gelimiteerde CPO van methaan in het vierkante reactiekanaal. Het model kan worden gebruikt om kinetische data te extraheren uit reactieselectiviteitsmetingen. In de microreactoren is er echter geen CPO van methaan uitgevoerd en slechts modelresultaten zijn gepresenteerd. Als helium in plaats van stikstof wordt gebruikt als inert gas in de voeding van de reactor, neemt de dichtheid en daardoor het Reynolds-getal af. Een lager Reynolds-getal resulteert in lagere lokale Sherwood-getallen. Ondanks de lagere Sherwood-getallen neemt de zuurstofconversie toe met 14%, omdat de diffusie van de componenten hoger is in het reactiemengsel met helium dan met stikstof. In het rekenmodel is de invloed van thermodiffusie meegenomen, omdat tussen de boven- en onderwand van het kanaal een temperatuurgradiënt van ongeveer 1.5 \times 10^6 \text{K/m} optreedt. Uit de berekeningen blijkt echter dat thermodiffusie nagenoeg geen effect heeft op de conversie en de veranderingen van oppervlakteconcentraties zijn niet meer dan 0.01%. De invloed van thermodiffusie is daarom verwaarloosbaar in het massatransportmodel, waardoor de modelberekeningen aanmerkelijk vereenvoudigen.

Microreactoren met een vlakke bovenwand hebben een beperkte operationele temperatuur van 870 K door elektrische doorslag van de siliciumnitridelaag in de bovenwand van het kanaal. Voor het stabiel uitvoeren van de katalytische partiële oxidatie van methaan moet de temperatuur in de reactor hoger zijn. Omdat p^{++}\text{Si} elektrisch geleidend is, zou het vermeden moeten worden in de buurt van de verwarimingselementen om elektrische doorslag te voorkomen. Microreactoren waarvan de bovenwand uit alleen SiRN of Si_3N_4 bestaat, zijn echter veel kwetsbaarder voor mechanisch falen door thermische spanningen. In een nieuw reactorontwerp zijn de verwarimingselementen opgehangen in geplooid SiRN buisjes. De SiRN buisjes vormen een geplooid zone waardoor mechanische spanning opgevangen wordt tijdens verwarmen. Deze reactoren zijn 110 uur lang gebruikt bij een temperatuur van 900 K. Bij hogere temperaturen beginnen de verwarimingselementen te degraderen, waardoor de levensduur terugloopt. Hoewel er geen katalytische reactie is uitgevoerd met deze reactor, is de verwachting dat deze reactoren gedurende enige uren stabiel kunnen werken bij een temperatuur van 1100 K. De verwachting is daarom dat door gebruik te maken van een reactor met opgehangen verwarimingselementen, de reactiekinetiek van de katalytische partiële oxidatie van methaan zal kunnen worden bestudeerd met een siliciummicroreactor.
Miniaturization of chemical process unit operations and reactors offers many fundamental and practical advantages to today’s chemical industry. In this chapter an introduction to these micro systems is given. Their advantages and disadvantages to chemical processing will be highlighted, followed by a literature survey on silicon based micro systems for various chemical unit operations. Subsequently, catalytic partial oxidation of methane and the advantages of using micro reaction technology for this particular reaction are discussed. At the end of this chapter, the background of the FORSiM-project, of which this research has been part, and the aim and outline of this thesis are provided.
1.1 Small dimensions in chemical processing

Micro system unit operations are defined as miniaturized unit operations fabricated, at least partially, by methods of micro technology or precision engineering. Micro systems typically contain flow channels in the sub-micrometer to the sub-millimeter range. Decreasing a length scale of a unit operation will decrease the distance for heat and mass transport. Next to this, decreasing a length scale will increase its surface area to volume ratio. In this way more exchange surface for heat and mass transfer per unit volume is provided. The most characteristic features of these small scale systems are highlighted in this section. Extensive reviews on micro-chemical-systems can be found in the books of Ehrfeld et al. [1], Hessel et al. [2], and Löwe et al. [3] and in articles of various authors [4–10].

Short characteristic length scales intensify heat and mass transport because the conduction and diffusion lengths are short as compared to those of large scale systems. A high heat transfer rate enables a direct control of the process temperature, e.g. fast preheating to the process temperature or cooling and quenching of reaction products to prevent the formation of unwanted side products. The high heat transfer rate in combination with small overall equipment size enables fast start-up and shutdown of the entire process. Fast start-up is a benefit for on demand production and fast shutdown will increase safety in case of failure. Down scaling a high temperature unit operation, can increase the temperature gradient between the inside and the outside of the unit proportionally. In that case, the construction materials will need to withstand large thermally induced mechanical stress. On the other hand, a large temperature gradient also gives a high driving force for heat transfer. Short diffusion lengths improve mass transport limited process rates and a large surface area to volume ratio enables a more efficient use of exchange surfaces for e.g. heterogeneous catalytic reactions and membrane processes. The throughput of the process can be increased per unit volume, by making more efficient use of these exchange surfaces.

Due to the small length scales, Reynolds numbers in micro systems are low, in the order of 1-1000 and therefore a laminar flow pattern will exist inside micro channels. Laminar flow can complicate mixing of different media. However,
to enhance mixing, the velocity field can be changed and the diffusion length decreased.

The small volume and precise geometry of micro structures can give a short and well-defined residence time. In this way, the residence time of the chemical process can be optimized, resulting in higher yield and higher reaction product selectivity compared to large scale systems.

Next to these process-yield and selectivity enhancing features, micro-chemical-systems are inherently safe. The high heat removal capabilities prevent hot spot formation. Runaway chain reactions like flames and explosions are averted. The short diffusion length scales promote the adsorption of free gas phase radicals at the walls and accordingly terminate these homogenous reactions. A micro structure can work as flame arrester in this way, preventing the propagation of flames and explosions. Moreover, in case of failure, the small hold-up of reactants will give less waste and low environmental impact.

The influence of erosion and corrosion on construction materials will have a larger impact on a micro system compared to a macroscopic system. The surface area to volume ratio and, inherently, the hydrodynamic properties of a micro system will change more drastically for a certain diameter change by erosion and or corrosion. The construction materials will need to be highly erosion / corrosion resistant or will need a protective coating. Although these materials are often more expensive and/or harder to utilize in a high precision fabrication process, less material is needed to build a micro system. Micro systems can therefore enable the use of exotic and costly materials [11].

Another advantage of micro-chemical-systems is the scale-up by scale-out or num-bering-up the system. The throughput of one single channel might be low, but by using more channels in parallel, production can easily be increased. Using micro structures with the same dimensions, no scale-up research is necessary, saving time and money on research. However, to ensure a good flow distribution between parallel micro-systems or inside a stack of channels, the relative difference between the channel diameters should be kept small [12] and also a flow distributor will be necessary.
As microreactor systems are small, they are very suitable for portable equipment e.g. production on the spot of hazardous chemicals, fuel processing, and analytical equipment. Their small overall size makes it easier to incorporate them into existing production processes and makes them very suitable for use in a laboratory e.g. for examination via high throughput screening to determine which catalyst or reaction conditions show the highest activity, and for reaction kinetic studies.

1.2 MEMS for chemical unit operations

Micro-electro-mechanical-systems (MEMS) are devices with characteristic dimensions in the sub-millimeter range. Devices can be made which combine electrical and mechanical components, by using integrated circuit batch-processing technologies. Using these production processes, known from the semiconductor industry, micro systems for chemical unit operations can be made from silicon and glass with very small dimensions. Silicon and glass devices essentially made by lithographic techniques have the advantage that structures can be made with a very high precision. Next to this, once a template is produced, it can be reused to produce identical replicate structures. Silicon and glass have the advantage above most metals that they are stable against corrosion at elevated temperatures [13]. Moreover, the high thermal conductivity of silicon can be a major advantage to avoid hot-spots inside a reactor and for heat exchange between exothermic and endothermic reactions. Inside a silicon micro device sensors and actuators may be integrated. In this way, fast and easy control of the conditions inside, instead of downstream of the micro device are possible. Stacking and bonding of silicon elements on top of each other are possible. In this way different unit operations can be added close to each other, avoiding dead volumes and making heat exchange between units possible [7, 14, 15]. In the following, a number of units in silicon based MEMS will be discussed, viz. mixers, separation devices, sensors, pumps, and reactors.

1.2.1 Mixers

Fabricating a mixer from silicon by means of lithographic techniques has the advantage that high precision 3-dimensional mixing structures can be produced.
In literature, different types of mixers are studied but comparing them is rather difficult because the mixing performance is quantified for different mixing processes and channel configurations.

As stated earlier, due to the small channel diameter, the Reynolds number in micro systems is usually low, and the flow pattern laminar. Mixing is therefore limited by diffusion, this in contrast with large scale systems where mixing is strongly enhanced by turbulence. The time needed for diffusion limited mixing is approximately:

\[ t_{\text{diff}} \approx \frac{d_{\text{lam}}^2}{D_A} \quad (1.1) \]

with, \( t_{\text{diff}} \) the diffusion time, \( d_{\text{lam}} \) the fluid lamella thickness, and \( D_A \) the diffusion coefficient in the mixture. \( D_A \) of gases is approximately 4 orders of magnitude larger than the \( D_A \) of a component in liquid. Mixing of liquids will therefore take \( 10^4 \) times longer than for gases. To reduce the diffusion time (\( t_{\text{diff}} \)), the fluid lamella thickness (\( d_{\text{lam}} \)) should be as small as possible.

One of the simplest configurations for mixing is the so called T-mixer, in which two streams are brought together in a T-configuration. Bökenkamp et al. [16,17] performed turbulent liquid mixing in T-shape mixers with Reynolds numbers up to 7900 and channel hydraulic diameter of 220 µm. However, mixing with high velocities will increase the pressure drop, especially in these channel structures. In a static T-mixer three different flow regimes are distinguished for liquid mixing by experiments and simulations [18]. Depending on the mixing effect, stratified flow, vortex flow, and engulfment flow are observed at laminar flow conditions. Mixing inside a channel after the fluids are brought together can be enhanced in different ways. Simply narrowing the channel i.e. reducing the width or height, the diffusion distance can be decreased [19]. Mengeaud et al. [20] enhanced mixing by using a zigzag channel, redirecting the flow, thereby introducing small disturbances in the flow pattern. At Reynolds numbers above 80, they found recirculations in the flow pattern which improved the mixing effect. Stroock et al. [21] showed that oblique ridges on the channel wall can cause helical flow inside a micro channel. In addition, a herringbone structure was introduced on one side of the channel, creating chaotic mixing [22]. Kim et al. [23] used the helical flow pattern to make a barrier embedded chaotic micro mixer. On one channel wall oblique ridges create the helical flow pattern.
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while on the opposite wall barriers are introduced to change the velocity field and realize mixing. More complex, 3-D mixer structures made from silicon reduce $d_{\text{lam}}$ by splitting and recombination and/or stretching and folding of the fluid to enhance mixing [24–27].

The advantage of the above mentioned passive mixers is that they have no moving parts. However, active mixing can be needed when diffusion is slow, the diffusion length is long, and/or in case of mixing batches. Bengtsson et al. [28] realized continuous active mixing inside micro channels using ultrasound. The ultrasound creates a rotating-vortex-flow or Rayleigh-flow inside the flow channel. In gene expression profiling assays, the sample solution is sandwiched between plates, creating long diffusion lengths for reagents which are added at the sides of the plates. Mixing of batch volumes down to 10 µl have been performed effectively by using a surface acoustic wave micro-agitation chip [29].

1.2.2 Heat exchangers

Heat exchangers made in silicon are well know as cooling for integrated circuits. The increasing power density in integrated circuits creates the need for improved cooling capacity [30, 31]. Silicon plates can be stacked and bonded together to form a plate heat exchanger [32]. The high thermal conductivity of silicon (148 J s$^{-1}$m$^{-1}$K$^{-1}$ at 300 K) can limit the efficiency of the heat exchanger due to high axial heat conduction inside the silicon [33]. This high thermal conductivity can be beneficial in preventing hot-spots and in case isothermal operation is required.

1.2.3 Separation devices

Micro machined separation devices can have the benefit of short diffusion pathways like micro mixers have. Due to the short diffusion length, the mass transfer between different phases can be increased. Next to this the high precision fabrication processes opens opportunities to processes which are very hard if not impossible to do in macroscopic separation devices. In literature, silicon based separation devices can be found for, filtering, stripping, extraction, acoustic separation, and membrane separation processes. Cross flow filters can be
used to prevent blocking of small channels by particles. The filter itself still clogs during operation but it can be successfully cleaned with a short back flush cycle [34]. A micro fabricated stripping column was built and operated by Cypes et al. [35] for the removal of toluene from water. The mass transfer capacity of the micro fabricated stripping process is nearly an order of magnitude higher compared to a packed column. This increase is the result of less resistance to mass transfer in the liquid phase due to the reduced thickness of the liquid film. Extraction of Co(II) in a counter-current flow system is used for Co(II) determination [36–38]. A stable liquid-liquid interface for the extraction process was maintained by making use of hydrophobic and hydrophilic surfaces and by using a guiding structure. Acoustic separation of lipid and red blood cells in blood plasma was performed in a continuous process by Petersson et al. [39]. Acoustic separation is based on the principle that particles either move towards a node or an anti-node of a standing wave, depending on their densities and compressibilities. Hydrogen purification with palladium membranes [40–42] is often studied for fuel cell applications or hydrogenation / dehydrogenation reactions. A well known problem with palladium membranes is hydrogen embrittlement. This problem can be overcome by making use of palladium-silver alloys [43]. Molecular size and shape selective membranes have been made by using zeolites [44, 45]. The advantage of these membranes is the possibility of incorporating catalytic properties to get a selective membrane reactor.

1.2.4 Sensors

Miniaturization of chemical sensors and analysis systems has the advantage of small sample sizes and thus less reagents are needed which are often toxic and/or expensive. Other advantages of the miniaturization of sensors are the fast analysis time, and the integration in other equipment as conventional systems and micro systems. Measurements in micro-sensors are often based on the detection of an electric resistance or capacity change. Below, some examples of these sensors are given, viz. temperature sensors, strain gauges, and chemical sensors.

Temperature sensors are made in different ways, micro scale resistance temperature detectors (RTD) and thermocouples [46, 47] have been fabricated. By
using temperature sensors and a heating element, flow rate detection can be performed [48–51]. Measuring a two-dimensional temperature distribution in a flow channel allows the simultaneous determination of flow velocity and fluid parameters like thermal conductivity, diffusion coefficient, and viscosity [52]. Another way of flow detection is by using a strain gauge [53, 54]. Metallic conductors subjected to mechanical strain exhibit a change in their electrical resistance. The change in capacitance, inductance, or resistance is proportional to the strain experienced by the sensor. The use of strain gauges has many applications e.g. measuring of pressure, acceleration, vibration, torque, and weight. Many small scale chemical sensors have been developed. These sensors are often made for applications in gas alarms and leakage detectors or are often part of a more complicated lab-on-a-chip analysis system including pumps, valves, and membranes. Most of these sensors are only suitable for specific analysis and samples of simple composition. In a conductometric sensor, the adsorption of gases on a thin film gives a change in the electrical conductance of the thin film which is detected [55–57]. Potentiometric sensors make use of current produced by a electrochemical reaction [58, 59]. The temperature rise of a catalytic combustion reaction is used to measure the concentration of combustion gasses in a calorimetric sensor [58, 59]. More complicated micro analyzers, suitable for many components are under development or have already been made like a micro gas chromatograph [60–62], a micro spectrometer [63, 64] a micro mass spectrometer [65, 66], and a micro hydrodynamic chromatograph [67].

1.2.5 Pumps

The pressure drop of the micro channels needs to be overcome to transport fluid through a micro fluidic device. This can be done by means of a pump. The basic principle consists of an oscillating diaphragm which increases and decreases the pump chamber volume [68, 69]. Back-flow can be prevented by adding valves, see Fig. 1.1, or by adding pumps in series. The most difficult issues for pumping within micro fluidic diaphragm pumps are the avoidance of dead volumes and bubble formation by cavitation. Next to the above described type of pump, pumping without moving parts can be done with electro-hydrodynamic and electro-osmotic pumps. In an electro-hydrodynamic pump, a fluid motion is achieved by using strong electrostatic forces, which are arranged to act on polar fluids [70]. In electro-osmotic flow, the charge difference in the electric
double layer near a surface is used to induce a fluid flow under the influence of an electric field [71, 72]. To pump gases without moving parts at low and high pressures, a Knudsen Compressor can be used [73, 74]. Pressures between 1.5 Pa and $10^{-5}$ Pa have been reached by using more compressor stages in series. Each stage is composed of a set of capillaries and a connector section, see Fig. 1.2. A temperature increase across the capillaries results in a thermal transpiration driven pressure increase. The capillary section is followed by a connector section where the pressure is approximately constant while the temperature drops to its original value entering the stage.

\[ \text{Figure 1.2: Schematic drawing of a one stage Knudsen compressor, flow direction from left to right. Temperature and pressure profile are indicated.} \]

### 1.2.6 Reactors

In chemical processes, the reactor is one of the most important parts. Most of the typical aspects of micro-chemical-systems, mentioned in section 1.1, are an
advantage for chemical reactions e.g. high heat and mass transport. As already mentioned, using silicon as a construction material makes it possible to incorporate sensors and actuators inside the micro structure. The different silicon based microreactors found in literature were therefore divided in two groups without and with sensors and actuators. In the following, some examples of these will be discussed briefly. Next to this, also attention will be given to catalyst deposition in these types of reactors.

1.2.6.1 Si-based reactors without heaters / temperature sensors

Silicon reactors without sensors and actuators are often heated externally by their reactor housing. In this way the reactors can be operated isothermally by making use of the high thermal conductivity of silicon, 148 J s$^{-1}$m$^{-1}$K$^{-1}$ at 300 K. A packed-bed reactor loaded with carbon particles was used for the phosgene production from chlorine and carbon monoxide [75]. Silicon oxide coating on the channel walls was used to prevent etching of the silicon reactor by chlorine. With this silicon based packed-bed reactor hot spots are suppressed by the increased heat transfer, resulting in a safe reactor operation. The direct fluorination of toluene was realized in a multi-phase microreactor [76]. Fluorine etches silicon, therefore the silicon channel walls are coated in this case with nickel to protect them. The high heat transfer inside the micro channels made it possible to execute the highly exothermic reaction safely at room temperature. Srinivas et al. [77] built a structured packed-bed reactor for preferential CO oxidation reaction over a Pt catalyst in a Al$_2$O$_3$ washcoat. The packed-bed of the reactor consisted of silicon pillars which give a mixed flow pattern through the entire reactor. Comparison with a conventional powder loaded packed-bed reactor showed similar operation characteristics. Porous silicon was used by Bengtsson et al. [78, 79] to improve the effective surface area of the flow channels in their enzyme microreactor. The porous silicon surface is reported to give a 350 times improved catalytic performance compared to a non-porous surface. Silicon microreactors incorporating different zeolites (Sil-1, ZSM-5 and Ts-1) were built by Wan et al. [44]. A silicon-glass microreactor with a TS-1 catalyst coating was used for 1-Pentene epoxidation reaction with hydrogen peroxide [80, 81]. Kusakabe et al. [82] made a reactor consisting of six parallel micro channels for screening different catalysts for the selective oxidation of carbon monoxide in hydrogen. The micro channels, 1 x 0.3 x 6 mm,
were filled with γ-alumina particles impregnated with Pt, Rh, Ru, Co, Ni, or Cu salts. Parallel screening was used to find that Pt was the most selective catalyst for CO oxidation [82]. Hydrogenation and dehydrogenation of cyclohexene to cyclohexane and benzene over a Pt catalyst was studied at 473 K by Besser et al. [83, 84]. The same reactor system was used for Fischer-Tropsch catalyst development and exploration of reaction mechanisms [85]. A membrane reactor for the dehydrogenation of cyclohexane to benzene was built by Cui et al. [41]. The reactor was equipped with a palladium membrane for hydrogen separation and a platinum catalyst on a titanium-oxide substrate.

1.2.6.2 Reactors with heaters / temperature sensors

Incorporation of sensors and actuators inside a system has the advantage of less dead volume compared to downstream measurement. Making use of heaters inside a microreactor system has the advantage that higher temperatures can be reached inside the reaction channel than at the outside of the reactor system. In this way degradation of seals at the inlet and outlet of the reactor and electrical connections can be prevented. A liquid phase microreactor with integrated liquid heat exchanger and temperature sensing was made for organic synthesis [86]. With the use of electric heaters, higher temperatures can be reached locally. Kusakabe et al. [87] used a Pt wire as heater for heating the reactants and the catalyst. Inside the reactor, sputtered Pt and a γ-alumina support impregnated with Pt were used for the catalytic hydrogenation of benzene at temperatures of 373 -523 K. The Pt heating wire can also be used as a catalyst by placing it inside the reaction channel. A catalytic heater was used by Veser et al. [88, 89] for the catalytic oxidation of hydrogen at temperatures up to approximately 1200 K.

Thin film heaters on a silicon based microreactor are often made by deposition of a platinum film. A trapezoidal channel was closed at one side by a thin wall containing a Pt catalyst on the inside and thin-film heaters and temperature sensors on the outside of the channel. A good thermal contact between the catalyst and the heaters and sensors is assured by the thin wall. In this way the reaction temperature can be controlled locally in an accurate way. Ammonia oxidation was executed in such a microreactor on a Pt-thin-film catalyst at 920 K [50, 51, 90–92]. CO combustion at 413 K was realized in a heated flow-
through membrane made of porous silicon [93]. The porous silicon was used as a support for the Pd catalyst and to thermally decouple the reaction zone from the rest of the reactor. A packed-bed reactor loaded with Cu / ZnO catalyst particles, was used for methanol reforming by Pattekar et al. [94]. The reactor was operated at 520 K with the incorporated heaters.

A gas-liquid-solid reaction, viz. the hydrogenation of cyclohexene over Pt / Al₂O₃ catalyst particles was performed in a silicon packed-bed reactor by Losey et al. [95, 96]. The thermal insulation of the reactor housing was tested and found to be very important for the reactor heating. With the heaters, a temperature of 573 K could be reached although the catalytic reactions were performed at room temperature. In two phase flow reactors, the overall mass transfer coefficient, \( K_{La} \) is an important parameter determining the process efficiency. A \( K_{La} \) of 5 - 15 s\(^{-1}\) was reported, which is about two orders of magnitude higher than in a trickle-bed reactor [96]. Different components for a micro fuel reformer are made by Tanaka et al. [97], consisting of an injector for air supply, catalytic butane combustor, heaters, methanol reforming reactor, and a polymer electrolyte membrane fuel cell. The different components were tested to adjust them for and incorporate them into a single micro device. A suspended-tube reactor consisting of SiRN tubes was made by Arana et al. [98, 99]. An advantage of this reactor is the thermal isolation to the surroundings and therefore high temperatures, up to 1200 K can be reached. A disadvantage of the good thermal isolation is the occurrence of run away reactions resulting in reactor failure. Although this silicon microreactor can be used for high temperature reactions, a major disadvantage is the increased complexity of the production process needed to build such a device.

### 1.2.6.3 Catalyst deposition

A major challenge in building microreactors is the incorporation of the catalytic material. For high selectivity and conversions, it is important to position the catalyst only at a specific position and not through the entire reactor system.

Catalyst deposition inside micro channels has been done in various ways. Different silicon microreactors are mentioned above [75, 95], which are loaded with catalytic particles. Inside these packed-bed reactors a filter structure is used to
keep the catalytic particles in place. The advantage is that virtually any solid catalyst can be prepared into particles. A disadvantage of this technique is the large pressure drop along the packed-bed.

Coating of the channel walls with the catalytic active material can be done. Deposition of the catalyst by impregnation of a wash coat is a well established process and has the advantage that many catalytic active materials can be deposited [100]. Surface area enhancing catalyst supports like alumina wash coating [98], porous silicon [78, 79, 93], or anodized alumina [101] can be used. Disadvantage of impregnation techniques are the positioning inside the channels [91, 98, 102]. Next to these coating techniques, zeolites have been used as catalyst inside silicon micro channels [44, 81]. Disadvantage of using zeolites are extra process steps needed in the fabrication process of a silicon based reactor system. Catalyst deposition by means of sputtering, using a shadow mask, makes the catalyst positioning very accurate [103] although the catalytic surface area will be very much less compared to the other mentioned techniques and, moreover, fewer catalytic materials are available for sputtering. Sputtered catalyst, therefore, can only be used for extremely fast reactions, in which only very small amounts of catalyst are needed for a high conversion in the microreactor. The reaction discussed in the next section is of this class.

1.3 Catalytic partial oxidation of methane in microreactors

Catalytic partial oxidation (CPO) of methane is a promising technology for efficient conversion of methane to synthesis gas. Synthesis gas, a mixture of hydrogen and carbon monoxide is one of the most important intermediates in the chemical industry. It is the main reactant in the Fischer-Tropsch process, in which gasoline is directly produced, and in the production of methanol. Next to this, synthesis gas can be used as a hydrogen source for various chemical processes. Production of hydrogen from synthesis gas, as needed in fuel cells, can be achieved after removing carbon monoxide. This can be done by the water-gas shift reaction, where CO is converted to CO$_2$ and additional hydrogen is produced. Subsequently, traces of remaining CO can be removed by selective CO oxidation, or purification by means of membrane technology [104, 105].
High temperature catalytic partial oxidation reactions have been shown to proceed with high conversion and selectivity over rhodium catalysts [106, 107]. The direct reaction pathway of synthesis gas production via direct partial oxidation is shown in reaction 1.2. Next to the direct partial oxidation, on a rhodium catalyst a two step reaction sequence of total oxidation of methane (reaction 1.3) and methane reforming with water and carbon monoxide to synthesis gas (reactions 1.4 and 1.5) is proposed [108]:

\[
\begin{align*}
\text{CH}_4 + 0.5\text{O}_2 & \rightarrow \text{CO} + 2\text{H}_2 \quad \Delta H_{298}^0 = -36 \text{ kJ/mol} \quad (1.2) \\
\text{CH}_4 + 2\text{O}_2 & \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad \Delta H_{298}^0 = -802 \text{ kJ/mol} \quad (1.3) \\
\text{CH}_4 + \text{H}_2\text{O} & \rightarrow \text{CO} + 3\text{H}_2 \quad \Delta H_{298}^0 = +206 \text{ kJ/mol} \quad (1.4) \\
\text{CH}_4 + \text{CO}_2 & \rightarrow 2\text{CO} + 2\text{H}_2 \quad \Delta H_{298}^0 = +247 \text{ kJ/mol} \quad (1.5)
\end{align*}
\]

These catalytic reactions can be described by a 38-steps reaction mechanism with adsorption, desorption, and surface reactions at the catalytic surface [108]. However, well known problems in determining the reaction mechanism for CPO are the temperature measurement at the catalyst [109], and mass transport limitations [110], which make the proposed reaction mechanism doubtful.

The catalyst temperature will determine the reaction rate and with the proposed combustion and reforming reactions which are exothermic and endothermic, temperature gradients along the reactor length can arise [109, 111]. The overall partial oxidation process is a very fast, mildly exothermic reaction. Hot spots and thermal runaway reactions can occur in case of bad heat transport from the catalyst. However, the improved heat transport inside microreactors can help to prevent hot spot formation and makes accurate control of the temperature possible. High surface area to volume ratio of micro channels also helps to overcome or reduce transport limitations to and from the catalyst. The transport limitations in the catalyst pores can be prevented by making use of wider pores or a non porous, flat surface catalyst coating on the micro channel walls.

Next to the above mentioned benefits, microreactors can be operated safely, even with explosive mixtures like hydrogen and oxygen [112]. Hydrogen, oxygen and nitrogen form flammable mixtures at almost all concentrations at room temperature. At higher temperatures the flammability region expands further.
From hydrogen oxidation experiments and modeling results it is found that flames and explosions are quenched inside small channels [113]. The suppression of flames and explosions in small channels is found to be a kinetic quenching of gas phase radicals at the channel walls due to improved mass transport rather than a thermal quenching mechanism due to an improved heat transfer rate. Because small channel reactors become intrinsically safe for explosive mixtures, reaction kinetic research can be performed at all concentrations even without dilution. An other advantage of gas phase radical quenching in narrow channels is the suppression of homogeneous reactions in heterogeneous reaction kinetic research.

1.3.1 Review of methane CPO microreactors

Recently various microreactors were made to convert methane and oxygen to synthesis gas. At Pacific Northwest National Laboratory (PNNL), Tonkovich et al. [114] developed a microreactor with a planar-sheet architecture. The microreactor consists of nine stacked stainless steel plates each with their own function in the process. In Fig. 1.3(a) a schematic representation of this microreactor configuration is given. Air is used as heat exchange fluid and is preheated at the bottom in a combustor heat exchanger. The hot air stream provides the heat to ignite the CPO reaction and preheats the cold reactants. At the top of the reactor, the reaction products are quenched in a third heat exchanger. Rhodium impregnated silica powder was used as catalyst in the channels (1500 x 254 µm) of the reaction plate. Non-equilibrium chemistry of the methane CPO reaction was found in this microreactor although sealing problems between the stacked plates and inaccurate temperature measurements were observed.

Stacking of platelets with channel structures in which the catalyst can be incorporated is a widely used way of making a microreactor. Instead of coating the channels with a catalytic active washcoat, the platelets can also be made of the catalytic material themselves. In the group of Schubert [11, 115] a microreactor was developed for methane CPO of stacked rhodium platelets, see Fig. 1.3(b). Although making a microreactor out of rhodium is expensive, rhodium has the advantage of a high thermal conductivity (120 Wm\(^{-1}\)K\(^{-1}\) at 1250 K), pre-
venturing hot spot formation on the catalytic surface. Two microreactors with different channel dimensions were made. The reaction channels of 120 x 131 x 5000 μm and 60 x 137 x 5000 μm were compared and comparable conversion and selectively were obtained. The results obtained with the different channel dimensions are a verification of the fact that, under reaction conditions, no mass transfer limitations will occur. The performance of the reactor was compared to literature values and it was mentioned that methane conversion and hydrogen selectivity were higher in the microreactor at comparable reaction conditions. The increased conversion and selectivity are likely to be caused by the absence of mass transport limitations, improved axial heat transport, and higher catalyst loadings.

Figure 1.3: (a) Schematic representation of the microreactor configuration of Tonkovich et al. [114], stacked platelets with different functionality. (b) Stacked Rhodium platelets forming the microchannels [11, 115].
A silicon based microreactor for the CPO of methane has recently been made by Younes-Metzler et al. [116]. A reaction channel of 1.5 x 0.2 x 10 mm is made and loaded with palladium catalyst in a Al$_2$O$_3$ wash coating. The channel is closed at one side by a Pyrex lid which allows temperature measurements with a IR-sensor. On the other side of the reactor, a piece of silicon is attached which is used as a resistive heater. In this way the complete microreactor chip is heated. Sealing of the gas inlet and outlet was done with golden o-rings to a ceramic block which is used for thermal insulation. Partial oxidation was performed by slowly increasing the reactor temperature. At 858 K the CPO reaction is ignited and due to the exothermic reaction a temperature increase to 888 K was measured. After ignition, carbon monoxide and hydrogen are formed but also catalyst deactivation due to carbon deposition is observed.

1.4 Scope and outline of this thesis

In this thesis the design of a silicon based microreactor for the catalytic partial oxidation (CPO) of methane is described. The work was performed as part of the STW FORSiM-project (Fast Oxidation Reaction in Si-technology based Microreactors) in which a feasibility study was executed to build and operate a silicon based microreactor with integrated sensors and actuators for CPO of methane. Although different microreactor systems have been studied in literature, the main challenge was to build a silicon based microreactor that could be operated at the relatively high reaction temperatures of 1100 K for high conversion and selectivity, and thereby aiming at a stable catalyst performance. Due to this high temperature, deterioration of gas and electric connections can be expected. A configuration was therefore chosen in which the temperature at these connections does not exceed 473 K. As a consequence of this a temperature gradient will exist in the reactor which will give rise to thermal stresses. As already mentioned before, correct temperature reading and, therefore, reaction parameter determination is difficult, due to the high temperatures and large amount of heat produced in the reaction [111]. Therefore, many aspects of the CPO reaction are up today not fully clear and application of the designed microreactor aims at kinetic research for this reaction. However, it should be noticed that such a reactor is applicable for the study of many fast heterogeneous reactions. The project was performed in close cooperation with the Transducers, Science
and Technology Group of the MESA+ Research Institute at the University of Twente.

In chapter 2 the activity and stability of spin coated and sputtered rhodium catalysts are studied, by making use of various flat silicon containing substrates (Si, Ta/SiO$_2$, SiO$_2$/Si, Si$_3$N$_4$/Si, SiRN/Si, and quartz). Deactivation of the rhodium is discussed.

Design aspects of the silicon based microreactor with integrated temperature sensors and heaters for catalytic partial oxidation reactions, are given in chapter 3. The hydrodynamic design, thermal design, catalyst, and electrical design of the heaters and sensors are presented. Safe hydrogen oxidation is demonstrated at temperatures up to 670 K.

In chapter 4 the results are presented of the simulation of heat and mass transport inside the micro channel based on computational fluid dynamics modeling. Semi-empirical Nusselt and Sherwood correlations for laminar flow are derived. These correlations are useful to decrease calculation times in kinetic research.

In chapter 5 a model is presented describing CPO of methane, including heat and mass transport inside the reaction channel. The influence of helium and nitrogen dilution, the Sherwood correlation used, and thermal diffusion are discussed.

A suspended heater reactor is presented in chapter 6. Previous reactor designs had a limited operation temperature of 870 K due to electrical breakdown. The suspended heater reactor was operated at temperatures above 1000 K without the electrical breakdown problems.

Finally in chapter 7 the main conclusions of this thesis and an outlook for useful improvements for high temperature silicon microreactors are given.
References


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Introduction


26 Introduction


Deactivation of rhodium catalyst on silicon substrates

Abstract
The catalytic activity and stability of rhodium, sputtered on different flat silicon containing substrates (Si, Ta/SiO₂, SiO₂/Si, Si₃N₄/Si, and SiRN/Si) have been studied. These substrate materials can be used in silicon-based microreactors as catalytic supports. The catalytic partial oxidation of methane (CPO) and the oxidation of hydrogen are studied on these substrates with sputtered rhodium as catalyst on top. All rhodium layers show an initially high catalytic activity with conversions close to 100%. However, for all layers, the conversion was found to decrease rapidly after 30-60 minutes and virtually no activity was found after 1-2 hours, independent of the composition of the interlayer. The mechanism of this deactivation was studied. Time-of-flight secondary ion mass spectrometry reveals that silicon is present on top of the rhodium layers after exposing the platelets to reaction conditions. In some cases rhodium is completely removed from the surface and is found in a subsurface layer within the silicon substrate. It is concluded that the silicon has diffused through the rhodium layer and is blocking the catalytic surface, resulting in deactivation of the catalyst.
2.1 Introduction

Micro-electro-mechanical-systems (MEMS) for chemical reactions are often used for studying heterogeneous catalytic reactions [1–8]. The base materials for producing these reactors are silicon, silicon oxide, and silicon nitride. Silicon oxide, SiO$_2$, and silicon nitride, Si$_3$N$_4$, are known refractory materials [9, 10] used for stable catalytic supports at high reaction temperatures. Next to these materials, low stress or silicon rich nitride (SiRN) layers have been used as catalyst supports in MEMS applications [1]. The catalyst can be deposited inside a MEMS device by means of impregnation of the support with the catalytic active metal, or by sputtering. An advantage of the impregnation technique over sputtering is the large variety of catalytic materials that can be used [11]. Moreover, a high specific catalyst area can be obtained by impregnation of a wash-coat. In contrast, the surface area of sputtered catalytic material is approximately equal to the geometric area. However, a disadvantage of wash-coating impregnation in MEMS is the difficulty of precise positioning of the catalyst inside a small (100-500 µm) reaction channel [12, 13].

Several different catalytic reactions have been executed successfully inside silicon based microreactors. For example, ammonia was catalytically oxidized to NO and H$_2$O. The reaction was carried out at 773 K for approximately 6 min on a 100 nm sputtered Pt catalyst on top of a 10 nm Ti / 1 µm SiRN layer [14]. A suspended-tube microreactor consisting of SiRN tubes wash-coated with Ir / γ-Al$_2$O$_3$ catalyst was used for hydrogen oxidation in combination with NH$_3$ cracking [13]. The reaction temperature was up to 1200 K for 3 minutes, reactor failure occurred due to a runaway reaction. Hydrogenation of benzene on a sputtered Pt catalyst is reported at 473-523 K for 150 hours, without reactor failure [3]. Explosive mixtures with H$_2$ and O$_2$ were safely oxidized on a 20 nm thick Rh catalyst deposited on a 30 nm SiO$_2$ layer on top of a 1 µm thick, heavily boron doped silicon layer. After 2 hours and 40 minutes, reactor failure occurred due to water condensation downstream of the reactor, see chapter 3.

MEMS-based devices with narrow channels are very suitable for catalytic reactions with high turn-over frequencies (TOF) and therefore very short residence times. This is because MEMS are well known for their high heat and mass transfer rates [15, 16], which can enhance the rates of mass and/or heat
transfer limited reactions. A well-known example of such a reaction is the catalytic partial oxidation (CPO) of methane over Pt or Rh catalyst, which has a reported TOF in the order of $1000 \text{s}^{-1}$ [17, 18]. High temperature (1100 K) CPO of methane to synthesis gas,

$$2\text{CH}_4 + \text{O}_2 \rightarrow 2\text{CO} + 4\text{H}_2,$$

has been shown to proceed with high selectivity over the above mentioned noble metal catalysts [19]. In the present study, the same reaction is carried out using rhodium as a catalyst, because it has an even higher selectivity than a platinum one.

Moreover, in MEMS applications, the adhesion of platinum on silicon layers is known to be problematic, since platinum peels off from the silicon surface. At high temperatures, too much stress is present in the platinum layer resulting in its detachment from the surface. Platinum is often used as a heater element with a titanium or tantalum interlayer as adhesion layer in MEMS applications. Tantalum interlayers are found to give a better adhesion than titanium interlayers for platinum on silicon [20]. Next to the platinum adhesion, tantalum might improve rhodium adhesion as well. However, it is unknown which influence the presence of this adhesive layer will have on the catalyst activity.

In the present study, different support materials, as can be used in MEMS production, are compared for their functionality, i.e. activity and stability as catalyst support material. Initially, CPO of methane was attempted at 1100 K. However at this high temperature peeling off of the rhodium layer and concomitant catalyst deactivation were observed. It was thought that the relatively high temperature of 1100 K was the main cause for this deactivation. Therefore the present study also focusses on the catalytic oxidation of hydrogen, as it can be executed at much milder reaction conditions, i.e. at 450 K.

Flat platelets of Si, SiO$_2$, SiRN, and Si$_3$N$_4$ were made with a sputtered or spin coated rhodium catalyst on top. Using these platelets as catalysts supports avoids making a complete MEMS, as this is a time consuming process. Similar thin catalytic layers on flat substrates such as SiO$_2$ and Al$_2$O$_3$, have been used in literature to study the catalyst support interactions of industrial cata-
Deactivation of rhodium catalyst on silicon substrates

The reaction conditions in an actual MEMS are mimicked by placing the platelets close to each other in a quartz reactor tube, in such a way that a rectangular micro channel of 500 µm depth is formed. As diffusion pathways will be very small in such system, this ensures that we have a very high heat and mass transfer, just like in a complete MEMS, as can be estimated from the appropriate Nusselt and Sherwood relations.

The influence of Si, SiO$_2$, SiRN, and Si$_3$N$_4$ as catalyst support materials and the presence of an adhesion layer (Ta) are investigated for the CPO of methane and for the catalytic oxidation of hydrogen on a Rh catalyst. Aside from avoiding the production of a full MEMS, using platelets has the additional advantage of easeing post-reaction analysis of the catalyst. This is especially of interest for the CPO reaction conditions, at which structural changes of the catalyst surface are found during reaction [22, 23]. The arrangement of platelets as a small rectangular channel enables the study of the effect of different gas residence times on the catalyst inside the reactor.

Thin film catalysts on electrical conducting substrates (e.g. Si) can be used for ion and electron spectroscopy techniques that are frequently used to yield information about e.g. elemental composition, the oxidation state of the catalyst, and whether or not elements on a surface are in contact with each other. In this study, the catalyst is examined by scanning electron microscopy (SEM), and time-of-flight secondary ion mass spectrometry (ToF-SIMS), to determine the structural and chemical changes of the different catalysts after being exposed to the reaction conditions.

2.2 Experimental

The model catalysts were made in two different ways, i.e. by means of sputtering and by means of wet chemical impregnation. Sputtered rhodium catalysts were prepared on silicon wafers at the MESA$^+$ Research Institute (University of Twente, The Netherlands) with interlayers of SiO$_2$, SiRN, or Si$_3$N$_4$. Next to these, catalysts prepared by sputtering, rhodium catalysts were deposited by wet chemical impregnation of a SiO$_2$ layer on a silicon wafer and of quartz
platelets with a RhCl$_3$ solution by spincoating.

2.2.1 Preparation of sputtered catalysts

After cleaning a p-type (100)-oriented silicon wafer in HNO$_3$, various intermediate layers were grown on the wafers. The SiO$_2$ (inter)layer was grown by dry oxidation, resulting in a SiO$_2$ layer of 154 nm. Interlayers of 215 nm Si$_3$N$_4$ and 206 nm Si$_3$N$_4$ were deposited by low pressure chemical vapor deposition (LPCVD) using SiH$_2$Cl$_2$ and NH$_3$ as precursors. Before a catalytic layer was sputtered on top of the grown layers, the wafers were cut into platelets of 3 x 8 mm$^2$. This was done to prevent the catalytic layer to peel off from the substrates during dicing. Sputtering of the catalytic layers was done with a base-pressure of 1·10$^{-6}$- 2·10$^{-6}$ mbar, and Ar pressure of 6.2·10$^{-3}$- 6.4·10$^{-3}$ mbar. Sputtering of Rh was done for 0.5, 1, 2, and 10 minutes, resulting in rhodium layers of approximately 6, 12, 24, and 100 nm, respectively. The platelets with 100 nm Rh were made with and without an adhesion layer of 10 nm Ta, sputtered on the substrates before the noble metal was deposited.

2.2.2 Preparation of rhodium catalyst by impregnation

Next to the sputtered catalytic layers, silicon platelets with a layer of silica and quartz platelets were impregnated with a rhodium catalyst. A one-side-polished p-type (100)-oriented silicon wafer was diced into platelets of 3 by 8 mm. After cleaning the platelets in isopropanol, they were calcined overnight at 1025 K to obtain a SiO$_2$ layer. The oxidized Si and the quartz platelets were cleaned by etching in a 1:1-mixture NH$_4$OH (30% ammonium hydroxide) and H$_2$O$_2$ (35% hydrogen peroxide) for 10 minutes at a temperature of 310-330 K. To introduce more surface hydroxyl groups after the etching procedure, the platelets were added to boiling deionized water for 20 minutes. After cooling the platelets in cold deionized water, they were spin coated under N$_2$ atmosphere with a 0.0135 molar RhCl$_3$·3H$_2$O solution in water at 293 K and 2800 rpm. From a spin coating model [24], the rhodium loading is predicted to be 11 atoms/nm$^2$. The actual catalyst loading is expected to be higher than the loading predicted by the model. This is because the model assumes the formation of a thin film due to the balance between centrifugal and shear forces on the catalytic solution used. However, in our experiments we observed droplets
on the small platelets because the liquid film could not spread out as the cen-
trifugal forces were smaller. To dry the platelets they were heated to 380 K for
1 hour and subsequently calcined at 670 K for 1 hour. Catalyst reduction and
chlorine removal was done by heating the platelets to the reaction temperature
with 50 vol% H\textsubscript{2} in He [25].

2.2.3 Experimental setup

The catalytic platelets, as described in the previous sections, are placed inside a
reactor tube made of quartz, schematically shown in Fig. 2.1. Two platelets can
be loaded into the holder, leaving a rectangular channel of 0.5 x 2 x 8 mm\textsuperscript{3}. The
reactor tube is heated by means of a tube furnace (Carbolite MTF 10/25/130) to
the reaction temperature. The reaction temperature is measured just above the
platelets inside the quartz platelet holder by means of a K-type thermocouple.
It was verified that the inlet gases are preheated to the reaction temperature be-
fore they reach the catalytic platelets. Next to this, the Si platelets have a high
thermal conductivity and will therefore equalize the platelet temperature and
ensure isothermal operation.

![Figure 2.1: Schematic drawing of the platelet holder, which is part of the reactor tube. At
the top: two platelets with the empty platelet holder; at the bottom: the platelets inside the
holder, leaving a rectangular micro channel of 0.5 x 2 x 8 mm.](image)

Analysis of the reaction products downstream of the reactor outlet is performed
by an on-line GC (Varian CP 3800) equipped with a Molsieve 5A column (for
separation of H\textsubscript{2}, O\textsubscript{2}, N\textsubscript{2}, CH\textsubscript{4}, and CO), a PoraPLOT U column (separation of
CO\textsubscript{2}, C\textsubscript{2}H\textsubscript{2} C\textsubscript{2}H\textsubscript{4}, C\textsubscript{3}H\textsubscript{6}, and H\textsubscript{2}O), and a TCD. Helium is used as carrier gas
and nitrogen as internal standard.

After the reaction experiments, the elemental and chemical composition of the
platelets surface were analyzed by ToF-SIMS analysis, using a IONTOF IV in-
instrument with a pulsed 15 keV Ga\textsuperscript{+} ion beam. The primary ion dose density was limited to 1\texttimes{}10\textsuperscript{13} atoms/cm\textsuperscript{2} (i.e. \approx 1\% of a monolayer) to ensure static conditions. ToF-SIMS depth profiling has been performed with dual beam in interlaced mode i.e. alternating sputtering (500 eV Ar\textsuperscript{+}) and analysis using time-of-flight detection of secondary ions.

## 2.3 Results / discussion

### 2.3.1 Catalytic partial oxidation of methane

The CPO of methane is performed on sputtered rhodium catalyst deposited on silicon platelets with different interlayers. Rhodium layers of 100 nm were used on top of SiO\textsubscript{2}, Si\textsubscript{3}N\textsubscript{4}, and SiRN interlayers. Both the SiRN and the SiO\textsubscript{2} interlayers were also used with a rhodium layer of 12 nm thickness. The effect of an adhesion layer on the catalytic reaction was tested by conducting an experiment with a tantalum layer underneath the rhodium catalyst. The experiments were performed by heating the platelets to 1073 K, with a temperature ramp of 10 K / min, in 10\% H\textsubscript{2} in He atmosphere for catalyst reduction. By adding oxygen to the gas mixture, and exchanging H\textsubscript{2} for CH\textsubscript{4}, the CPO reaction was started. In table 2.1 the results of the measurements are shown, together with the reaction conditions temperature (\(T\)), residence time (\(\tau\)), and CH\textsubscript{4} to O\textsubscript{2} ratio in the feed. Next to the reaction conditions, the results are presented of oxygen conversion (\(X_{O_2}\)), methane conversion (\(X_{CH_4}\)), hydrogen selectivity (\(S_{H_2}\)), carbon monoxide selectivity (\(S_{CO}\)), selectivity for C\textsubscript{2}-molecules (\(S_{C_2}\)), and Rh coverage on the surface by means of a visual inspection of photos taken from the platelets after the reaction. The experimental results for conversion and selectivity shown in the table are values off the initial 15 minutes of an experiment. During all experiments, the catalytic activity decreased in time and after 1 hours on stream no catalytic activity was observed anymore. In Fig. 2.2 the oxygen conversion as a function of time is shown for the 12 and 100 nm Rh on top of a SiRN interlayer. The oxygen conversion and therefore the catalytic activity of the 12 nm Rh layer starts lower than for the 100 nm Rh layer and both show a decrease in time. The strong decrease in time of the catalytic activity was found for all catalytically active platelets. Because a strong decrease in the catalytic activity was observed, the reactor temperature was increased up
Table 2.1: Conversion and selectivity for CPO of methane on silicon platelets, covered with differed interlayers

<table>
<thead>
<tr>
<th>interlayer</th>
<th>SiO₂</th>
<th>SiO₂</th>
<th>Ta / SiO₂</th>
<th>Si₃N₄</th>
<th>Si₃N₄</th>
<th>SiRN</th>
<th>SiRN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh (nm)</td>
<td>12</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>12</td>
<td>100</td>
</tr>
<tr>
<td>T (K)</td>
<td>1098</td>
<td>1103</td>
<td>1059</td>
<td>1099</td>
<td>1121</td>
<td>1100</td>
<td>1099</td>
</tr>
<tr>
<td>(\tau) (ms)</td>
<td>3.5</td>
<td>1.2</td>
<td>1.2</td>
<td>2.6</td>
<td>2.6</td>
<td>2.3</td>
<td>2.5</td>
</tr>
<tr>
<td>CH₄/O₂ (%)</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1</td>
<td>2.1</td>
</tr>
<tr>
<td>He (%)</td>
<td>87</td>
<td>78</td>
<td>78</td>
<td>88</td>
<td>88</td>
<td>87</td>
<td>82</td>
</tr>
<tr>
<td>(X_{O_2}) (%)</td>
<td>1.2</td>
<td>93</td>
<td>5.8</td>
<td>99</td>
<td>99</td>
<td>41</td>
<td>97</td>
</tr>
<tr>
<td>(X_{CH_4}) (%)</td>
<td>2.7</td>
<td>26</td>
<td>0.3</td>
<td>44</td>
<td>43</td>
<td>20</td>
<td>57</td>
</tr>
<tr>
<td>(S_{H_2}) (-)</td>
<td>0</td>
<td>0.45</td>
<td>0</td>
<td>0.28</td>
<td>0.41</td>
<td>0</td>
<td>0.72</td>
</tr>
<tr>
<td>(S_{CO}) (-)</td>
<td>0.1</td>
<td>0.70</td>
<td>0</td>
<td>0.88</td>
<td>0.96</td>
<td>0.07</td>
<td>0.80</td>
</tr>
<tr>
<td>(S_{C_2}) (-)</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.23</td>
<td>0</td>
</tr>
<tr>
<td>coverage*</td>
<td>++</td>
<td>-</td>
<td>++</td>
<td>-</td>
<td>-</td>
<td>++</td>
<td>+</td>
</tr>
</tbody>
</table>

* ++ platelet is for 100 - 90 % covered with a metallic layer,
  + platelet is for 90 - 70 % covered with metal,
  - platelet is for 70 - 40 % covered with metal,
  -- platelet is for 40 - 0 % covered with metal.

Increasing the temperature increased the conversion and selectivity to \(H_2\) and CO, i.e. synthesis gas, except for 12 nm Rh on SiO₂, 100 nm Rh on Ta / SiO₂, and 12 nm Rh on SiRN. However, after about 1 hours on stream at a temperature of 1100 K no catalyst activity was observed and no \(H_2\) or CO was formed anymore for all platelets. Comparing the results of the platelets with a SiO₂ interlayer, only the platelets with a 100 nm Rh layer showed activity towards \(H_2\) and CO. The thinner Rh layer of 12 nm did not show any activity to synthesis gas although the catalyst coverage of this thin layer was much better on visual inspection. Also the use of Ta as an adhesion layer between the SiO₂ and the Rh improved the sticking of the catalyst to the platelets, but, as in the case of the thin Rh layer no catalytic activity was found. The catalyst on the Si₃N₄ interlayer showed activity to \(H_2\) and CO but the metal layer peeled off from the substrate which may explain the decrease in catalytic activity. The results from the experiments with the SiRN interlayer showed an initial high conversion and selectivity for the 100 nm Rh layer.

Comparing the 100 nm to the 12 nm Rh layers, the sticking of the thicker Rh
layers to the different interlayer was less. After the experiments it was visually observed that rhodium was lost from some of the substrates, see table 2.1. Under CPO conditions, most of the 100 nm Rh layers peel off from the substrate due to stress in the material. The rhodium lost from the substrates was found as small Rh particles downstream in the platelet holder. Although the temperature downstream of the platelet holder is lower than in the platelet holder, rhodium can still catalyze the complete oxidation of H\textsubscript{2} and CO and therefore may decrease the measured selectivity towards them. Overall the thicker Rh layers showed a higher conversion and selectivity to synthesis gas compared to the thinner Rh layers. The thinner Rh layers and the use of the Ta adhesion layer showed a better sticking to the substrate but less catalytic activity.

Despite differences in selectivity and activity, the different interlayers had one thing in common: a deactivation of the catalyst within 1 hour. The relatively high reaction temperature (1100 K) could be the cause of this deactivation due for example diffusion, reactions of the catalyst with the interlayer, and / or peeling of Rh from the surface. Therefore, the CPO experiments were abandoned and the catalytic hydrogen oxidation (at 473 K) was attempted using the same
2.3.2 Hydrogen oxidation

The catalytic oxidation of hydrogen $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ can be operated at milder reaction conditions (i.e. 450 K) than CPO of methane (1100 K). The catalytic hydrogen oxidation reaction was studied on similar platelets.

To avoid non-catalyzed gas phase hydrogen oxidation in the reactor, the temperature for spontaneous oxidation was determined by using blank silicon platelets inside the platelets holder. The flow rate to the reactor was 1.2 mmol/min consisting of 4% $\text{O}_2$, 12% $\text{H}_2$, and 84% He. The oxygen conversion by gas phase reactions was determined at the outlet of the reactor while the reactor temperature was slowly increased. At a temperature of about 300 °C (573 K), the gas phase reactions were initiated, setting the upper temperature for the catalytic hydrogen oxidation experiments.

Catalytic hydrogen oxidation was performed on silicon platelets using three different interlayers. Platelets with an interlayer of SiRN with sputtered rhodium of 6, 12, and 24 nm and both SiO$_2$ and Si$_3$N$_4$ interlayers with 12 nm of rhodium were used. Next to sputtered rhodium catalyst, spin coated rhodium on SiO$_2$ on top of silicon and on quartz platelets was used. In Fig. 2.3 the oxygen conversion as a function of time is shown for all platelets, sorted by type of interlayer. In all cases, the initial activity of the catalyst is high, resulting in conversions of $\text{O}_2$ of nearly 100%. All platelets showed a decrease in catalytic activity during hydrogen oxidation in time. The decrease in activity follows more or less the same behavior for all sputtered layers: an initially high conversion is followed by a sharp decrease after 30 to 60 minutes of reaction. After 1-2 hours, virtually no remaining catalytic activity of the sputtered layers is observed. In contrast, the spin coated layers do not show the rapid decrease in catalytic activity. The activity decreases gradually in time and significant conversion is still measured after 5 hours. The spin coated layer on silicon oxide (Fig 2.3(a)) has a lower initial activity than the sputtered layers but its long term activity is much higher. The spin coating on quartz shows an initially high conversion rate that decreases relatively slowly. The main difference between the quartz platelets and the SiO$_2$/Si platelets is the absence of the silicon layer un-
Figure 2.3: Oxygen conversion during hydrogen oxidation reaction as a function of time on stream. Rhodium layers thicknesses given in the figures are all for sputtered layers. Reaction conditions: $T = 473$ K, He = 30 ml/min, $N_2 = 1$ ml/min, $H_2 = 3$ ml/min, $O_2 = 1$ ml/min STP.

(a) 12 nm Rh / 154 nm SiO$_2$ / Si and spin coated Rh on top of SiO$_2$ / Si and quartz.
(b) 12 nm Rh / 206 nm Si$_3$N$_4$ / Si.
(c) 6 nm Rh, 12 nm Rh or 24 nm Rh / 215 nm SiRN / Si.
Deactivation of rhodium catalyst on silicon substrates
derneath the SiO$_2$. The Rh layer thickness on SiRN interlayers is compared in Fig 2.3(c). No distinct difference between the layer thickness and deactivation time is found. During the hydrogen oxidation experiments no loss of catalytic material due to peeling off from the substrates was observed. Comparing the deactivation time of the CPO and hydrogen oxidation experiments, the deactivation during the CPO is faster. The faster deactivation can be caused by the temperature difference and the different reactants used.

2.3.3 Platelets surface analysis by SEM and ToF-SIMS

During CPO of methane and catalytic hydrogen oxidation, catalyst deactivation is observed for most of the tested platelets. Deactivation of the platelets takes 1 - 2 hours except for the spin coated quartz platelets. The fast deactivation of the platelets cannot be explained by contaminations from the setup as stable operation is possible as can be seen in Fig. 2.3(a). Therefore, it was concluded that the catalytic deactivation was apparently caused by changes in the platelets during the experiment. Morphology changes of the catalytic surface were studied with scanning electron microscopy (SEM). Additionally, the chemical composition of the deposited layers prior to and after the reactions was analyzed with time-of-flight secondary ion mass spectrometry (ToF-SIMS).

2.3.3.1 SEM

It turned out to be difficult to make reliable SEM images of the unused Rh surfaces because the Rh surface is very smooth. Focusing of the electron beam of the SEM was only possible at rarely occurring defects, such as the crack in the rhodium surface on top of a Si$_3$N$_4$ platelet as shown in Fig. 2.4. The Rh surface was still very smooth after the catalytic hydrogen oxidation experiments, comparable with Fig. 2.4.

Figure 2.5 shows the SEM image of the surface of a 100 nm Rh on 10 nm Ta / 154 nm SiO$_2$ / Si platelet after a 2 hour use as catalyst in CPO, using the conditions given in table 2.1. It shows Rh and/or Ta agglomerated particles with a diameter in the order of 1 µm. Similar agglomeration was found for Pt on Ti and Ta adhesion layers, as used for heating elements in MEMS [20]. It was found that these Ti and Ta adhesion layers were oxidized and ended up
Figure 2.4: SEM image of surface of an unused 100 nm Rh on Si₃N₄/Si platelet before the catalytic reactions. The smooth Rh surface is visible as the gray area, the dark line is one of the very rare defects in the Rh layer, showing the Si₃N₄ substrate.

in the valleys between the coalesced Pt structures. This is very likely to occur for the Rh layer as well. The Rh left on the 100 nm Rh / 154 nm SiO₂ / Si and 100 nm Rh / 206 nm Si₃N₄ / Si platelets after CPO conditions as given in table 2.1 is shown in Fig. 2.6. Compared to the Rh left on the Ta / SiO₂ inter-layer more spongy structures are found. The spongy surface structure was also found for the Rh remaining on the platelets with a SiRN interlayer, as shown in Fig. 2.7. During the SEM analysis of the SiRN platelets, a difference between the middle and the side of the platelets was observed. In Fig. 2.7 the difference

Figure 2.5: SEM images of 100 nm Rh on 10 nm Ta / 154 nm SiO₂ / Si platelet after CPO of CH₄ with a 1000x and 10000x enlargement; experimental conditions, see table 2.1. The white spots are the Rh and/or Ta agglomerates.
between the Rh structure at the sides and in the middle of a platelet is shown. When platelets are loaded into the quartz reactor, the side parts of the platelets are covered by the quartz holder shown in Fig. 2.1. In Fig. 2.7(b) it can be seen that the side of the platelet has a more dense structure compared to the middle of the platelet, Fig. 2.7(d). The surface structure differences may be caused by small gas phase composition differences. At the sides of the platelets, covered by the quartz holder, the surface is less accessible to the reactant gases in the CPO reaction, whereas formed product gases such as CO can only be removed by diffusion.

It is known from literature, that under the influence of oxygen containing gases the Rh surface morphology can change. Fichtner et al. [23] observed small crystallites on the Rh surface. These crystallites were only formed at the inlet of their reactor made of Rh-foil under CPO conditions. For platinum gauzes used in industry, roughing of the surface is a well known phenomenon. This roughing or reconstruction is associated with the reaction itself as it does not occur at reaction temperature in the presence of either one of the reactants alone [22].
Results / discussion

(a) Side of platelet, enlargement: 1000x.
(b) Side of platelet, enlargement: 10000x.
(c) Middle of platelet, enlargement: 1000x.
(d) Middle of platelet, enlargement: 10000x.

Figure 2.7: SEM images of 100 nm Rh on 215 nm SiRN / Si platelets after CPO $CH_4$; experimental conditions, see table 2.1. The light gray areas are the Rh catalyst parts which are left on the SiRN surface. The dark area is the SiRN layer, except in (b) and (d) in which the dark area’s are parts which are out of focus in the SEM image.
2.3.3.2 ToF-SIMS

Examination of the platelets by ToF-SIMS reveals the chemical composition of the catalytic layers and can therefore gain more insight in the mechanism of the deactivation. In Fig. 2.8 the secondary ion intensity as a function of time, i.e. depth of 12 nm Rh / 215 nm SiRN / Si platelets as deposited is shown. As can be seen in Fig. 2.8, the outer surface (time = 0 s) consists mainly of rhodium. At a depth of approximately 11 nm (time = 150 s) the relative ion intensity of silicon becomes higher than the relative ion intensity of rhodium. This is approximately the place where the rhodium layer ends and the SiRN substrate begins. The relatively high Si intensity at time = 0 s indicates silicon-components at the outer surface of the platelets. The oscillations in the Si and Si$_2$N signals in the substrate are caused by sample charging. The depth profile of the unused platelet looks quite similar to the depth profile made of a platelet after deactivation during hydrogen oxidation. Therefore, the signal intensity ratios of Si to Rh fragments (I$_{Si}$ / I$_{Rh}$) and SiO to Rh$_2$ fragments (I$_{SiO}$ / I$_{Rh_2}$) are compared instead, before and after hydrogen oxidation reaction conditions, see Figs. 2.9(a) and 2.9(b). From these figures it can be seen that after hydrogen oxidation the I$_{Si}$ / I$_{Rh}$ and I$_{SiO}$ / I$_{Rh_2}$ ratios at the outer surface have increased. This indicates

Figure 2.8: Relative secondary ion intensity as a function of time i.e. depth profile of 12 nm Rh / 215 nm SiRN / Si platelet as deposited. The time scale corresponds with a depth of approximately 25 nm.
Figure 2.9: Signal intensity ratios $I_{\text{Si}} / I_{\text{Rh}}$ and $I_{\text{SiO}_2} / I_{\text{Rh}_2}$ as a function of sputtering time before and after hydrogen oxidation reaction of 12 nm Rh / 154 215nm SiRN / Si platelet. The time scale corresponds with a depth of approximately 4.3 nm.

a silicon enrichment at the outer surface under hydrogen oxidation reaction conditions. In Fig. 2.10 the depth profile of a 12 nm Rh / 215 nm SiRN / Si platelet is shown after CPO of methane up to a temperature of 1233 K. It can be seen that after CPO a more or less constant density of Si and SiO$_2$ is found on the platelet. No remaining SiRN is found in the spectrum up to about 500 s, corresponding to a depth of approximately 35 nm, therefore it is concluded that the SiRN was oxidized to SiO$_2$. Virtually no Rh is left on the top layer of the platelet, where it was originally deposited in a layer of 12 nm thickness. Instead, the first significant rhodium amount is found at a depth of approximately 30 nm. No loose rhodium particles where found in the reactor tube and therefore the rhodium was not lost by peeling from the substrate. Apparently the rhodium has diffused into the oxidized SiRN layer or, alternatively, silicon or silicon containing compounds have diffused through the rhodium layer. The spectra of a rhodium layer sputtered on a SiO$_2$ interlayer show similar features. Silica diffuses through the rhodium layer or vice versa, resulting in complete coverage of the Rh catalyst.
Figure 2.10: Secondary ion intensity as a function of time i.e. depth profile of 12 nm Rh / 215 nm SiRN / Si platelet after CPO of CH₄ up to 1233 K. The time scale corresponds with a depth of approximately 65 nm.

Also a ToF-SIMS analysis was done on the spin coated platelets. No depth profile can be made of these platelets, as the spectrum would contain a large amount of substrate contribution i.e. the ion intensity of the substrate like silicon containing compounds would predominate over the Rh catalyst ion intensities. Using ToF-SIMS imaging (25 keV pulsed Ga⁺ beam), the Si and Rh ion mapping are visualized, and shown in Fig. 2.11. In this figure light areas contain the compound mentioned underneath the figure, dark areas contain other compounds. Comparing the Si ion and Rh ion mapping, Figs. 2.11(a) and 2.11(b), of the as deposited platelet, it is found that Rh particles mask the silicon containing substrate. After exposing the platelet to hydrogen oxidation conditions, the silicon compounds are found all over the platelet, also on the places were Rh is detected, see Figs. 2.11(c) and 2.11(d). This corresponds to the ToF-SIMS depth profiles of the SiRN and SiO₂ interlayers, where silicon is also covering the rhodium layer. In the literature review by Min et al. [26], on Pd catalytic layers on top of SiO₂ / Si substrates similar effects were reported. Pd silicides were formed at the SiO₂ / Si interface after inter-diffusion of Pd into the substrate via oxygen vacancies. The silicide formation enhances the inter-diffusion process, resulting in complete coverage of the metal surface. Using a SiO₂ / Mo
substrate i.e. leaving out the Si substrate, it was found that Pd-silicide formation is initiated by a trace of Si. An excess of Si accelerates the silicide formation and influences the composition of the silicide. Silicon contaminations inside a Pd foil were found to migrate to the surface and deactivate the Pd catalyst under the influence of H₂O at 598 K in 40 min [27]. This time is in the same order of magnitude as the deactivation times found in this study for the catalysts deposited on silicon containing substrates. In the ToF-SIMS depth profile of the as deposited rhodium layer, Fig. 2.8, it can be seen that inside the Rh layer, silicon was present. Diffusion of silicon and silicides under the influence of H₂O and H₂ to the rhodium surface, like on a palladium surface, might result in blocking of the catalytic sites, causing the deactivation in time. Silica migration has also been found on Pt/SiO₂ at 660 K [28] and Co/SiO₂ catalyst at 493 K [29].

However, in a recently built silicon MEMS-based device, no catalyst deactivation was found after 2 hours and 40 minutes, as described in chapter 3. It can be argued that in this silicon-based reaction system doping levels and dopants are very different from these applied in the silicon substrates used in this chapter. The dopant concentration of the p-type silicon platelets is 1-3·10¹⁵ atoms cm⁻³, as compared to 2-4·10¹⁹ atoms cm⁻³ for the top wall of the above mentioned MEMS-based device. Next to the doping level, the catalyst supporting wall
in the MEMS-based device experienced thermal stress during operation which can also influence the diffusion processes.

The 100 nm Rh layers initially showed catalytic activity for CPO which is very likely due to the fact that these thick layers had formed a porous structure under the influence of the high temperature, see Fig. 2.7. It can be expected that under the influence of the increased temperature the rhodium - silicon diffusion process becomes faster. However, the catalyst deactivation times for both the hydrogen oxidation (1-2 hours) and the CPO (1 hour) reaction were in the same order of magnitude. It should be mentioned, however, that the porous structure formed has less contact with the Si-containing substrate and therefore the diffusion of silicon is likely to be slower.

### 2.4 Concluding remarks

The behavior of sputtered and spin coated Rh catalysts is studied, by making use of different interlayers grown on top of flat silicon substrates (Ta/SiO$_2$, SiO$_2$/Si, Si$_3$N$_4$/Si, and SiRN/Si). Rh catalysts on the different supports are used for hydrogen oxidation (473 K) and CPO of methane (1000 - 1200 K). During both reactions, catalyst activity is measured in time. For both reactions and for most substrates an initial high conversion is observed. However, after 1-2 hours on stream, no catalytic activity can be observed any more, for most of the substrates, and for both reactions. ToF-SIMS experiments revealed that during both hydrogen oxidation and CPO reactions, the Rh catalyst becomes covered with silicon containing components by diffusion from the substrates. The silicon diffusion to the outer surface of the catalytic layer explains the catalyst deactivation during time on stream for Rh.

In semiconductor industry, diffusion barriers are often used to prevent the diffusion of different layers into each other. These diffusion barriers might influence the catalytic reactions and the high temperature stability of these layers is still an issue of research. The quartz platelets used did not show deactivation. However, these are less suitable for surface science/research as they are not electrically conducting. In high temperature silicon based microreactors, Al$_2$O$_3$ wash-coatings have been used [13]. The Al$_2$O$_3$ wash-coatings form
porous structures which can prevent or slow down the silicon diffusion into the catalyst. For the purpose of examining the catalytic structural surface changes, \( \text{Al}_2\text{O}_3 \) wash-coatings are not suitable, as they do not have a smooth catalytic surface. A possible solution to study the catalytic surface may be found in the combination of a porous wash-coating or anodic oxidized \( \text{Al}_2\text{O}_3 \) [30] with a flat sputtered catalytic layer on top of it.

Acknowledgement

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References


Deactivation of rhodium catalyst on silicon substrates


References


Design of a silicon-based microreactor for catalytic oxidation reactions

Abstract

A silicon-based microreactor for catalytic oxidation reactions has been designed and tested. The reactor design is based on a square reaction channel with a length of 2 cm and a hydraulic diameter of 500 µm, closed at one side by a thin flat channel top wall. The channel top wall supports heaters and temperature sensors that are in close contact with the catalyst which is positioned at the reverse of the thin top wall. A model is made to calculate the temperature profile in this thin top wall. The calculation results show that most of the heat supplied with the heaters is lost by conduction through the top wall. The thinner the top wall and the smaller the meandering heaters are made, the more efficient the heating becomes. This thermal model is validated with experiments performed with three microreactor prototypes. The operation window of the third microreactor prototype, i.e. the prototype with the thinner top wall and smaller meandering heaters, is limited to 870 K. The maximum temperature is limited due to electrical breakdown of the channel top wall. The microreactor is tested for catalytic hydrogen oxidation. Flammable mixtures of hydrogen and oxygen were used at temperatures of 560 - 670 K, proving the safe operation of the microreactor.
3.1 Introduction

In this chapter the design considerations for and experiments with a silicon-based microreactor are discussed. The objective is to build and operate a silicon-based microreactor, with integrated sensors and actuators, which can be used as a tool to study the reaction kinetics of an exothermic oxidation reaction, such as the catalytic partial oxidation (CPO) of methane. Next to this, the reactor can also be useful for small-scale production of hydrogen for fuel cells. The CPO reaction products viz. hydrogen and carbon monoxide can be made usable for fuel cells by removing carbon monoxide by means of the water gas shift reaction followed by selective CO oxidation or purification by means of membrane technology.

The small length scales of microreactors make them well suited for fast reactions like CPO that need short residence times and reaction product quenching by heat exchange to prevent over-oxidation. The short length scales will enhance heat and mass transfer and can therefore improve heat and mass transfer limited reaction rates [1]. Next to these advantages, microreactors are very suitable for handling explosive gas mixtures like methane or hydrogen in combination with oxygen [2], because flames and explosions can be quenched inside the micro channels.

The design of the microreactor starts from published layouts of silicon-based microreactors, as found in literature. An overview of some of the characteristics of silicon-based reactors, sorted on their operation temperature is given in table 3.1. In most of these reactors, the reaction channel is closed at one side by a thin silicon or silicon nitride wall. In figure 3.1 a representative sketch of such a reactor is given, showing the flow channel, heaters, temperature sensors, and catalytic layer. The functionality of this thin layer is to ensure a good thermal contact between the heaters and sensors on top of it and the catalyst, which is deposited underneath it at the inside of the channel. The heaters only heat part of the reactor to the reaction temperature of 1100 K in case of methane CPO, while the rest of the reactor chip is maintained at a lower temperature. In this way degradation of electrical and gas connections is prevented. The last two reactors mentioned in table 3.1 have a more complicated structure than the others: they both have more than one heated channel side. Heat removal from the
reaction gases is lower when more channel side walls are heated. In case of an
explosion or run-away reaction the heat removal in such reactors can become
insufficient, resulting in reactor failure [14].

The long term aim is to build a microreactor for CPO of methane, $2\text{CH}_4 + \text{O}_2 \rightarrow 2\text{CO} + 4\text{H}_2$. This catalytic reaction gives high conversion and selectivity to
CO and H$_2$ (synthesis gas) at a temperature of 1100 K over a rhodium catalyst
[15, 16]. Difficulties in operating a silicon microreactor can be expected when
performing a reaction at high temperatures like deformation of the thin top wall
[17]. This paper is therefore restricted to hydrogen oxidation, $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$,
as this test reaction can be operated at a lower temperature of 450 K. In this way,
the functionality of the microreactor design and experience with its operation
are explored to be able to carry on to the CPO reaction.

## 3.2 Reactor design

An overview of the design criteria for a silicon-based microreactor with a thin,
heated, and catalytically active top wall as sketched in Fig. 3.1 are given in this
section. As already mentioned, the microreactor should be able to execute CPO
of methane to synthesis gas whereas it should also be possible to perform reac-
tion kinetic studies on this reaction. CPO of methane gives high conversion and
selectivity over a rhodium catalyst at a temperature of 1100 K with a reported
turn-over frequency in the order of 1000 s$^{-1}$ [15, 18].

The cross-sections of the channels used in literature often have a trapezoidal
shape with the most narrow side being the thin top side of the channel. In
the present study, a square channel cross-section is chosen for modeling conve-
Table 3.1: Silicon microreactors with heaters and sensors on a thin wall

<table>
<thead>
<tr>
<th>temp. (K)</th>
<th>reaction</th>
<th>catalyst</th>
<th>channel geometry</th>
<th>$d_h^1$ (µm)</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>520</td>
<td>methanol reforming</td>
<td>Cu</td>
<td>trapezoidal</td>
<td>507</td>
<td>[3]</td>
</tr>
<tr>
<td>520</td>
<td>methanol reforming</td>
<td>Cu/ZnO</td>
<td>rectangular</td>
<td>570</td>
<td>[4]</td>
</tr>
<tr>
<td>920</td>
<td>NH$_3$ oxidation, methanol</td>
<td>Pt</td>
<td>trapezoidal</td>
<td>627</td>
<td>[5–9]</td>
</tr>
<tr>
<td>970</td>
<td>dehydrogenation</td>
<td>Na</td>
<td>trapezoidal</td>
<td>520</td>
<td>[10]</td>
</tr>
<tr>
<td>970-1070</td>
<td>methanol dehydrogenation</td>
<td>Na</td>
<td>rectangular, 2</td>
<td>525</td>
<td>[11]</td>
</tr>
<tr>
<td>1203</td>
<td>butane oxidation, ammonia</td>
<td>Pt Ir</td>
<td>heated rectangular, isothermal</td>
<td>280</td>
<td>[12–14]</td>
</tr>
</tbody>
</table>

1 hydraulic diameter $d_h = \frac{4 \times \text{cross-sectional area}}{\text{wetted perimeter}}$
2 no reaction results presented
3 pack bed reactor, particle size 50-70µm
4 coated and/or sputtered catalytic wall
5 homogeneous catalyst
6 washcoat with γ-Al$_2$O$_3$ on posts and walls

Siicon-based microreactor design

The heaters of the reactor are used to heat the feed gases in a preheating section, see section 3.2.2.4, and to heat the catalyst to the reaction temperature. Catalyst temperature is crucial in reaction kinetic studies and therefore the temperature
profile of the thin top wall is determined, see section 3.2.2.1. Next to the reaction products hydrogen and carbon monoxide, water and carbon dioxide can be formed. Water and carbon dioxide formation can be expected at places where the catalyst temperature is low. The catalyst should therefore be deposited with great care, to prevent these low temperature catalytic reactions, see section 3.2.3. The catalyst length is determined to ensure a short residence time at the catalyst and to ensure the CPO reaction not going to equilibrium in case of kinetic studies. In case water is formed by the reaction, condensation on the channel side walls should be prevented. Therefore the entire silicon reactor chip is heated to a temperature of at least 350 K, see section 3.3.3. The heaters will preheat the top wall up to 1100 K, whereas the side walls of the channel are kept at 353 K. Thermal stresses will occur, due to this temperature difference over the width of the channel top wall. The mechanical stability is discussed in section 3.2.4.

3.2.1 Hydrodynamic design

A characteristic of microreactors are their small channel diameters. When the flow system’s characteristic length becomes comparable to the molecular mean free path ($L$) the continuum assumption is no longer valid, because a thermodynamic non-equilibrium at the gas-solid interface can exist (slip-flow and temperature jump) [20–22]. The flow regimes, deviating from continuum behavior, can be classified with the Knudsen number ($Kn$), as shown in table 3.2. $Kn$ is defined by:

$$Kn = \frac{L}{d_h}$$

in which $L$ is the average distance traveled by an atom or molecule of a gas between collisions and $d_h$ is a representative physical length scale, the hydraulic diameter $d_h = \frac{4 \times \text{cross-sectional area}}{\text{wetted perimeter}}$.

<table>
<thead>
<tr>
<th>Knudsen number</th>
<th>flow regime</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Kn \leq 0.001$</td>
<td>Continuum flow</td>
</tr>
<tr>
<td>$0.001 &lt; Kn \leq 0.1$</td>
<td>Slip-flow regime</td>
</tr>
<tr>
<td>$0.1 &lt; Kn \leq 10$</td>
<td>Transition regime</td>
</tr>
<tr>
<td>$10 &lt; Kn$</td>
<td>Free-molecule flow</td>
</tr>
</tbody>
</table>
The depth of the square channel is determined by the silicon wafer thickness of 500 µm, due to advantages in the production procedure of the reactors [23]. At low Knudsen numbers, collision processes dominate and the flow remains in local thermodynamic equilibrium, L is defined by [24]:

\[ L = \frac{\mu}{\rho} \left( \frac{\pi M}{2RT} \right)^{1/2} \] (3.2)

For nitrogen at a temperature of 1100 K and atmospheric pressure i.e. for conditions that resemble CPO conditions, it is found that \( Kn = 6 \times 10^{-4} \). Therefore, it is clear that the continuum flow regime can be assumed and traditional fluid dynamic equations such as the Euler and Navier-Stokes equations can be used when modeling a microreactor with \( d_h = 500 \mu m \).

The flow pattern in macroscopic channels can be expected to be laminar when the Reynolds number (\( Re \)) is small, \( Re < 2000 \) [25]. For smooth micro channels it is reported that the transition from the laminar to the turbulent flow region is at about the same order of magnitude \( 1500 < Re < 2000 \) [26, 27]. The channel walls in our reactor will be smooth, because the channel is made in silicon by etching. Using representative values for CPO of methane, \( Re \approx 150 \). The flow regime in the silicon microreactor can therefore be considered as laminar.

Axial dispersion of components is negligible when the Peclet number (\( Pe \)) or Bodenstein number (\( Bo \)) > 100 [28]. In case of the CPO reaction, \( Pe > 100 \) and therefore axial dispersion can be neglected giving a short residence time distribution on the laminar flow profile.

### 3.2.2 Thermal design

In this section the thermal design of the reactor is considered. The inlet gases of the reactor are preheated and the catalyst is heated to ignite the CPO reaction at \( T \approx 830-1000 K \) [29] with the heaters. The heaters and sensors have a good thermal contact with the catalyst because they are separated by a thin, \( \approx 1 \mu m \), layer of silicon, which has a high thermal conductivity (148 W m\(^{-1}\)K\(^{-1}\) at 300 K). A heat balance is made in section 3.2.2.1 to calculate the temperature profile in the top wall and accordingly in the catalyst. In this heat balance, the electrical
input of the heaters and heat losses by conduction and convection are considered. The different heat losses from the top wall are compared in section 3.2.2.2. The thermal response time of the reactor is examined in section 3.2.2.3. A short heat-up time of the reactor allows a quick start-up for on demand production. A short cool-down time of the reactor enables a fast shut-down in case of failure. The channel length to preheat the feed gases to the reaction temperature is determined with a heat balance over the length of the channel in section 3.2.2.4.

3.2.2.1 Temperature-profile in the heated top wall

A heat balance of the thin top wall is made to calculate the heater power needed to reach the reaction temperature. This model is also needed to correct the temperature readings of the sensors. The sensor reading is an average of all temperature values along the contact between the sensor and the top layer surface. It is possible to correct for this averaging once we can predict the lateral temperature profile of the top wall.

A cross-section of the top wall is considered with the different heat transfer mechanisms, see Fig. 3.2. Heat transfer by conduction to the side walls is expected to be higher than by natural convection and forced convection, because of the high thermal conductivity of silicon. Considering the width of the channel, \( d_h = 500 \, \mu m \) and the thickness of the top wall \( \delta = 1 - 3 \, \mu m \), heat conduction over the thickness of the top wall is neglected. This means that the top wall temperature \( (T_t) \) is assumed to be uniform over the top wall height \( (\delta) \). Taking the length \( l = 0.02 \, m \), as derived in section 3.2.3, and the width of the channel \( d_h = 0.0005 \, m \), the channel top wall is 40 times longer than its width. Therefore heat transfer by conduction is expected to be mainly towards the side walls of the channel as this distance is shorter. Heat is generated in the channel top wall by electrical input in the heaters. Heat is lost from the top wall by natural convection or conduction to the environment, forced convection to the gasses
flowing through the channel, and conduction to the side walls. Heat loss by radiation is neglected, although it could be substantial at the high temperatures needed in the CPO reaction of 1100 K. This assumption is validated with calculations presented later in section 3.2.2.2. Heat loss by radiation is calculated to be less than 5% of the total heat losses.

The result of the above assumptions is a 1-dimensional model of the top wall, schematically shown in Fig. 3.3. The origin of the x-axis is taken at the middle of

![Figure 3.3](image)

Figure 3.3: (a) Sketch of channel top wall cross-section, with \(d_h\) the hydraulic diameter of the channel, \(\delta\) the height of the top wall \(w_H\) the width of the heater, \(l_H\) the length of the heater, and \(x\) the coordinate over the width. (b) Sketch of channel top wall cross-section, with the surrounding temperatures, \(T_t(x)\) the top wall temperature as function of the channel width, \(T_i\) the temperature at the channel side walls, \(T_o\) the temperature at the outside of the channel, and \(T_i\) the temperature at the inside of the channel.

The corresponding stationary heat balance, over the width of the channel, is given by:

\[
\begin{align*}
&l_H \delta \left( -\kappa \frac{dT_t}{dx} \bigg|_x + \kappa \frac{dT_t}{dx} \bigg|_{x+\Delta x} \right) + \frac{P}{w_H} \Delta x (1 - U(x - \frac{w_H}{2})) - \\
&h_{\alpha}(T_t - T_o)l_H \Delta x - h_{\beta}(T_i - T_l)l_H \Delta x = 0
\end{align*}
\]

The heater power \((P)\) is assumed to be equally distributed over the heater width \((w_H)\) and length \((l_H)\). In a first reactor design the length of a heater element \((l_H)\)
is chosen 4.1 mm. At the sides of the top layer, the temperature is assumed to
be equal to the temperature of the side walls \( T_s \), see Fig. 3.3(b). In Eq. 3.3 \( \kappa \)
is the thermal conductivity of the top wall, \( U(x - \frac{wh}{2}) \) is a unit step function.
The heat transfer coefficients \( h_o \) and \( h_i \) are for outside and inside the reactor
respectively, \( T_o \) is the gas temperature outside and \( T_i \) the gas temperature inside
the reactor. Eq. 3.3 is rewritten, by making use of a dimensionless coordinate
\( \hat{x} = \frac{2x}{dh} \), the fraction heated in the top layer \( \varepsilon = \frac{wh}{dh} \), the total heat transfer
coefficient \( h_{\text{tot}} = h_o + h_i \), the average gas temperature \( T_g = \frac{h_o T_o + h_i T_i}{h_o + h_i} \), and by
substitution of \( \hat{T}_t = T_i - T_s \) and \( \hat{T}_g = T_g - T_s \) to:

\[
\frac{d^2 \hat{T}_t}{d\hat{x}^2} + \alpha (1 - U(\hat{x} - \varepsilon)) - \beta (\hat{T}_t - \hat{T}_g) = 0
\]

(3.4)

in which

\[
\alpha = \frac{Pdh}{4\delta \kappa l_H}
\]

(3.5)

and

\[
\beta = \frac{h_{\text{tot}} d_i}{4\delta \kappa}
\]

(3.6)

whereas the boundary conditions are:

\[
\hat{x} = 0 \quad \frac{d\hat{T}_t}{d\hat{x}} = 0
\]

(3.7)

\[
\hat{x} = 1 \quad \hat{T}_t = 0
\]

(3.8)

The temperature profile inside the channel top layer is solved by Laplace trans-
formation, which results in:

\[
T_t = A \cosh(\sqrt{\beta} \hat{x}) - \frac{\alpha + \beta (T_g - T_s)}{\beta} \left( \cosh(\sqrt{\beta} \hat{x}) - 1 \right) + \frac{\alpha}{\beta} \left( \cosh(\sqrt{\beta} (\hat{x} - \varepsilon)) - 1 \right) U(\hat{x} - \varepsilon) + T_s
\]

(3.9)

with:

\[
A = \frac{\alpha \cosh(\sqrt{\beta}) - \cosh(\sqrt{\beta}(1 - \varepsilon))}{\cosh(\sqrt{\beta})} + (T_g - T_s) \frac{\cosh(\sqrt{\beta}) - 1}{\cosh(\sqrt{\beta})}
\]

(3.10)

The heat losses by convection and the heat conductivity of the top layer must
be known to calculate the temperature along the top wall of the channel, with
Eqs. 3.5, 3.6, 3.9, and 3.10. The convective heat loss at the outside ($h_o$) and at the inside ($h_i$) of the reactor are determined in appendix 3.A. Outside the reactor the convective heat loss is found to be by conduction only, giving $h_o \approx 10$ Wm$^{-2}$K$^{-1}$. Inside the reaction channel forced convection is dominant giving $h_i \approx 375$ Wm$^{-2}$K$^{-1}$. In fact, the top wall of the channel is made as a composite wall for mechanical stability, see section 3.2.4. The top wall consists of 0.15 µm SiRN or 0.2 µm Si$_3$N$_4$ and 0.85 µm p$^+$ Si, giving for $\delta \approx 1$ µm. The thermal conductivity of the top wall is calculated in appendix 3.B, taking into account the composite material and the temperature dependence of the heat conductivity.

The temperature of the top wall is shown in Fig. 3.4 for different heater powers ($P$) and relative heater widths ($\varepsilon$) as a function of the dimensionless coordinate $\lambda = \frac{x + 1}{2}$, i.e. the origin defined at the left side wall. Heaters across the complete top wall width ($\varepsilon = 1$), shown in Fig. 3.4(a), use more energy to reach about the same temperature than smaller heaters at a lower supply power ($P$) as shown in Fig. 3.4(b). The gradual temperature profile from the middle to the side walls is mainly caused by the large heat conduction in the top wall as proven in the next section.

3.2.2.2 Heat loss from the top wall

The energy losses from the top wall are compared to each other to see what the main heat loss mechanism is. The energy loss by conduction through the top wall to the side walls is defined by: $Q_{\text{con}} = 2q \int_{x=1}^{x=1} \delta_l H$ in which $q \mid_{x=1}$ is the heat loss from the top wall by conduction to a side wall defined as:

$$q = \frac{\kappa}{d_h} \frac{d^2 T_t}{dx^2} = \frac{2\kappa}{d_h} \frac{d^2 T_t}{dx^2}$$

$$= 2\kappa \left( \frac{A - \alpha + \beta(T_k - T_l)}{\beta} \right) \sqrt{\beta} \sinh \left( \sqrt{\beta}x \right) +$$

$$\frac{\alpha}{\beta} \sqrt{\beta} \sinh \left( \sqrt{\beta(x - \varepsilon)} \right)$$

(3.11)

Heat loss from the top wall by natural convection and forced convection is calculated with respectively: $Q_{\text{nat}} = l_H d_h h_o (T_t - T_o)$ and $Q_{\text{for}} = l_H d_h h_i (T_t - T_l)$. In Fig. 3.5(a) the relative heat flow rates are shown in a Sankey diagram. From
Figure 3.4: (a) The temperature profile in the channel top wall as a function of the dimensionless channel width ($\lambda$) and a heater power of $P = 1.0$ W, $P = 1.5$ W, and $P = 1.7$ W ($\varepsilon = 1$). (b) The temperature profile in the channel top wall as a function of the dimensionless channel width ($\lambda$) for a relative heater width of $\varepsilon = 0.3$, $\varepsilon = 0.5$, and $\varepsilon = 1.0$ ($P = 1$ W). The calculations are performed for a microreactor with a top wall existing of 0.15 µm SiRN and 0.85 µm $p^{++}$ Si.

This figure it can be seen that for 1 W of heater power and a relative heater width $\varepsilon = 0.3$, 75.2 % of the energy provided by the heaters is lost by conduction. Because most of the energy provided by the heaters is lost by conduction, the thinner the top wall the less heat is lost and the higher the temperature inside the top wall becomes. On the other hand, using a thinner channel top wall will make it more fragile. An other way to reduce the heat loss by conduction and consequently increase the top wall temperature is to decrease the relative heater width, see Fig.3.5(b). Next to $Q_{con}/P$, the maximum temperature i.e. the temperature in the middle of the top wall ($T_{max}$), the average temperature over the width of a heater ($T_{h}$), and the average top wall temperature($T_{t}$) are shown in Fig 3.5(b). A decreasing value of $\varepsilon$, leads to increasing $T_{max}$, $T_{h}$, and $T_{t}$.

To check the assumptions and to verify the analytical results, we have created a 2-dimensional FEMLAB (finite elements) model [30] of the reactor top wall.
Figure 3.5: Calculation results for a microreactor with a top wall of 0.2 µm Si₃N₄ and 0.85 µm p⁺⁺Si, ε = 0.3, and P = 1 W. (a) Sankey diagram of the channel top wall showing the relative heat flow rates. (b) The maximum temperature ($T_{\text{max}}$), average heater temperature ($T_h$), average top wall temperature ($T_t$), and the relative energy loss ($Q_{\text{loss}}/P$) by conduction through the top wall as a function of the relative heater width.

This model explicitly takes into account that the top wall is composed of different layers. The analytical model approximates its average thermal conductivity $\kappa$ as described in appendix 3B. The analytical model neglects heat loss by radiation whereas the FEMLAB model does not, so we use the latter to verify that radiation is indeed negligible.

A large temperature gradient exists in the top wall because the width is small $d_h = 500$ µm. Also the aspect ratio of the channel top wall is large, $d_h/\delta = 500$, therefore many grid cells are needed to get the heat balance solved correctly. In the 2-dimensional model, 18000 grid cells were needed to get the summation of the overall heat balance on all boundaries correct, i.e. equal to 0.

To take radiative heat loss to the environment ($Q_{\text{rad}}$) into account, heat flow
Reactor design

by radiation for a gray-body emitter is assumed [31]:

$$Q_{\text{rad}} = \sigma e l_l d_h (T^4 - T_g^4)$$  \hspace{1cm} (3.12)

in which $\sigma = 5.67 \times 10^{-8}$ Wm$^{-2}$K$^{-4}$, the Stefan-Boltzmann constant, and $e = 0.7$, the emissivity [14]. In Fig. 3.6(a) the relative heat flow rates calculated with the 2-D FEMLAB model of solid heat conduction $Q_{\text{con}}/P$, forced convection $Q_{\text{for}}/P$, natural convection $Q_{\text{nat}}/P$, and radiation $Q_{\text{rad}}/P$ as a function of the power $P$ dissipated in a heater with $\varepsilon = 0.3$, are shown. Heat loss by radiation

![Figure 3.6: Calculation results for a microreactor with a top wall of 0.2 µm Si$_3$N$_4$ and 0.85 µm p$^{++}$Si, $\varepsilon = 0.3$, and $P = 1$ W. (a) Different relative heat flow rates from the channel top wall as a function of the supplied heater power. (b) Comparison of the maximum top wall temperature calculated with Eq. 3.9 (1-D model) and FEMLAB (2-D model) as a function of heater power, with $\varepsilon = 0.3$.](image)

($Q_{\text{rad}}$) becomes significant i.e. $> 5 \%$, at $P > 1.5$ W, leading to $T_{\text{max}} > 1150$ K as shown in Fig. 3.6. At lower temperatures, the heat loss is mainly caused by solid heat conduction and forced convection.

In Fig. 3.6(b) the maximum temperature calculated with the FEMLAB 2-D model is compared to the 1-D model result as given by Eq. 3.9. A deviation $> 5 \%$ occurs at $P > 0.9$ W. As already mentioned, the only differences between these two models are inclusion/exclusion of radiation heat losses and the treatment
of $\kappa$ of the $p^{++}$Si layers. Neglecting $Q_{\text{rad}}$ and the temperature dependence of $\kappa$ in solving the heat balance Eq. 3.9 gives a good prediction of the top wall temperature up to a heater power of $P \approx 0.9$ W. At $P \approx 0.9$ W the maximum temperature in the top wall becomes $T_{\text{max}} \approx 800$ K which is sufficient for hydrogen oxidation.

### 3.2.2.3 Thermal response time

Fast heat-up and cool-down times of the reactor give fast start-up, shut-down, and quenching of the chemical processes inside the reactor. Fast start-up is an advantage for on demand production. Fast shut-down increases safety in case of reactor failure. Fast quenching of the CPO reaction products, hydrogen and carbon monoxide, can prevent the oxidation to water and carbon dioxide.

Making use of the earlier defined dimensionless top wall width ($\hat{x}$), the total heat transfer coefficient ($h_{\text{tot}}$), and the average gas temperature ($T_g$), the transient heat balance for any power distribution over the channel width ($P(\hat{x})$), is defined by:

$$\frac{4l_H\delta\kappa}{d_l} \frac{\partial^2 T_t}{\partial \hat{x}^2} + \frac{P(\hat{x})}{\varepsilon} - h_{\text{tot}} l_H d_h (T_t - T_g) = \rho c_p l_H d_h \frac{\partial T_t}{\partial t}$$

(3.13)

in which $\rho$ is the top wall density, $c_p$ the mean top wall heat capacity, and $t$ the time. Rewriting 3.13 with the dimensionless number $\beta$, as defined in Eq. 3.6 and a dimensionless time $\theta = \frac{4\alpha t}{\rho c_p d_h}$ gives:

$$\frac{\partial^2 T_t}{\partial \hat{x}^2} + \frac{P(\hat{x})d_h}{4\delta\kappa l_H} - \beta (T_t - T_g) = \frac{\partial T_t}{\partial \theta}$$

(3.14)

The heat balance after heating to a steady state temperature ($T_{ss}$) becomes:

$$\frac{d^2 T_{ss}}{d\hat{x}^2} + \frac{P(\hat{x})d_h}{4\delta\kappa l_H} - \beta (T_{ss} - T_g) = 0$$

(3.15)

Introducing the temperature change $\hat{T} = T_{ss} - T_t$ and subtracting Eq. 3.14 from Eq. 3.15 gives:

$$\frac{\partial^2 \hat{T}}{\partial \hat{x}^2} - \beta \hat{T} = \frac{\partial \hat{T}}{\partial \theta}$$

(3.16)
Reactor design

This equation is solved with the following boundary conditions:

\[
\begin{align*}
\hat{T} &= 0 \quad \text{at } \hat{x} = 1 \\
\frac{\partial \hat{T}}{\partial \hat{x}} &= 0 \quad \text{at } \hat{x} = 0
\end{align*}
\]  

(3.17) 

(3.18)

to give:

\[
\hat{T} = \sum_{n=1}^{\infty} \eta_n \cos \left( \frac{2n-1}{2} \pi \hat{x} \right) \exp \left( - \left( \frac{2n-1}{2} \pi \right)^2 + \beta \right) \theta 
\]  

(3.19)

At \( \theta = 0 \), i.e. \( t = 0 \), the top wall temperature \( T_t \) is equal to the temperature of the side wall \( T_s \) for all values of \( \hat{x} \); \( \hat{T}(\hat{x}) = T_{ss}(\hat{x}) - T_s \).

\[
T_{ss}(\hat{x}) - T_s = \sum_{n=1}^{\infty} \eta_n \cos \left( \frac{2n-1}{2} \pi \hat{x} \right)
\]  

(3.20)

At the middle of the channel, \( \hat{x} = 0 \) and \( T_t \) has a maximum. For all practical purposes, \( T_t \big|_{\hat{x}=0} \) is well approximated by the first term in the series expansion in Eq. 3.19 to give \( \eta_1 \big|_{\hat{x}=0} = T_{ss} \big|_{\hat{x}=0} - T_s \), leading to:

\[
T_t \big|_{\hat{x}=0} \approx T_{ss} \big|_{\hat{x}=0} - (T_{ss} \big|_{\hat{x}=0} - T_s) \exp \left( - \left( \frac{\pi^2}{4} + \beta \right) \theta \right)
\]  

(3.21)

or

\[
\frac{T_t \big|_{\hat{x}=0} - T_s}{T_{ss} \big|_{\hat{x}=0} - T_s} \approx 1 - \exp \left( - \frac{t}{\tau} \right)
\]  

(3.22)

in which \( \tau \) is the time constant of the heat-up process. \( \tau \) is the time needed for \( T_t \big|_{\hat{x}=0} \) to reach 63.2% of \( T_{ss} \big|_{\hat{x}=0} \), which can be calculated from Eqs. 3.21 and 3.22:

\[
\tau = \frac{\rho \sigma d_t^2}{1 + \frac{h_{tot} d_t^2}{\gamma \pi \kappa}} \approx 0.49 \text{ ms}
\]  

(3.23)

Fast heat-up and cool-down within the millisecond range is feasible with the microreactor. At about 4.6\( \tau \approx 2.3 \) ms the reactor top wall will reach its steady state temperature within 1%. 

3.2.2.4 Channel length to preheat inlet gases

Inside the reaction channel, the inlet gases are preheated before they reach the catalyst. The channel length needed to preheat the feed gases is calculated with a stationary heat balance over the channel length.

\[
m \frac{\partial c_p T_g}{\partial z} = N_u_t \frac{k}{d_h} (T_t - T_g) + N_u_{sb} \frac{k}{d_h} (T_s - T_g)
\]  

(3.24)

in which \(m\) is the specific mass flow rate, \(c_p\) the heat capacity, \(T_g\) the average gas phase temperature, \(z\) the length coordinate of the channel, \(k\) the heat conductivity of the gas, \(a_{v,t}\) and \(a_{v,sb}\) the specific surface areas of the top wall and of the side and bottom walls respectively, \(d_h\) the hydraulic diameter of the channel, \(N_u_t\) the Nusselt number at the top wall, and \(N_u_{sb}\) the average Nusselt number of the side and bottom walls. The Nusselt numbers are defined for different channel side wall temperatures in chapter 4 [32]. These Nusselt correlations are described with the temperature ratio \(R\):

\[
R = \frac{T_s - T_{in}}{T_t - T_s}
\]

(3.25)

in which \(T_{in}\), \(T_s\), and \(T_t\) are respectively the temperature of the inlet, the side wall, and the average of the channel top wall. As the inlet gases and the side walls of the channel are heated by the microreactor housing, \(T_{in} = T_s\) and \(R = 0.\)

The Nusselt correlations for laminar flow in a square channel heated from the topside with \(R = 0\) are [32]:

\[
N_u_{t,R=0} = 4.69 \left(1 + \frac{G_{zh}}{233}\right)^{0.809}
\]

(3.26)

\[
N_u_{sb,R=0} = 0.40 - 1.96 \tanh\left(7.3G_{zh}^{-0.64}\right) + 5.11 \tanh\left(17.9G_{zh}^{-0.44}\right)
\]

(3.27)

In Eqs. 3.26 and 3.27 the Graetz number for heat transport \((G_{zh})\) is used as a dimensionless length of the reaction channel defined as:

\[
G_{zh} = Re Pr \frac{d_h}{z}
\]

(3.28)
Reactor design

with \( Pr \) the Prandtl number. \( T_g \) is calculated iteratively from Eq. 3.24 and plotted in Fig. 3.7 as function of the channel length \((z)\) for different values of \( T_e \). CPO of methane is executed at a temperature of 1100 K leading to \( T_t \approx 800 \) K.

![Figure 3.7: Average gas phase temperature \( T_g \) as function of the reactor length coordinate \((z)\) for different average top wall temperatures \((T_t)\) at a gas inlet velocity of 10 ms\(^{-1}\).](image)

The complete development of the temperature results in \( T_g \approx 490 \) K, as can be seen in Fig. 3.7. A channel of 0.026 m is required to preheat the gases to 99\% of the temperature the gases would reach inside an infinitely long channel. This requires a rather long preheating section in the reactor. Therefore 95\% temperature development is chosen which requires a preheating section of 0.012 m.

### 3.2.3 Catalytic layer design

The catalyst is situated on the top wall at the inside of the channel, as was shown in Fig. 3.1. In this way the heaters and sensors are in close contact with the catalyst for respectively preheating the catalyst and measuring the catalyst reaction temperature. Hydrogen oxidation will be executed inside the microreactor to explore its functionality, although ultimately the reactor is to be used for CPO of methane. As described below, the catalyst is designed for the CPO reaction because the CPO reaction puts more constraints on the catalytic layer than hydrogen oxidation.

Hydrogen oxidation and catalytic partial oxidation of methane can both be executed on platinum and rhodium catalysts [15, 18]. In this thesis rhodium is used for the silicon microreactor system. Rhodium compared to platinum gives the
highest conversion of methane and the highest selectivity to synthesis gas. Next to these advantages, Rh-oxide does not sublime like Pt-oxides do at high temperatures. For instance, PtO$_2$ sublimes at $T > 673$ K [33], leading to an unstable catalytic reaction system.

For CPO of methane, the turn-over frequency can be in the order of 1000 s$^{-1}$ [15, 18]. Measuring intrinsic reaction kinetics requires a diffusion time scale of the reactants to the catalyst ($\tau_{\text{dif}}$) to be shorter than the reaction time scale.

$$\tau_{\text{dif}} \approx \frac{d_h^2}{\pi D_{AB}}$$  \hspace{1cm} (3.29)

in which $D_{AB}$ is taken as the diffusion coefficient of O$_2$ in N$_2$ at the average gas temperature. The average gas temperature ($T_g$) under CPO conditions is calculated in section 3.2.2.4, $T_g = 490$ K. This implies the height of the channel should approximately be $d_h < 380$ µm, in order to get a diffusion time which is at least comparable to the chemical time scale of CPO. However, for practical reasons $d_h = 500$ µm (see section 3.2.1), and accordingly the diffusion of the reactants to the surface can be expected to be rate limiting. Reaction kinetics can therefore only be observed from the reaction selectivity, which is determined by the ratio of chemical rate coefficients instead of by the coefficients themselves. For that purpose, the reaction should not have 100% conversion, because in that case chemical equilibrium will be reached. In the following, the length of the catalyst ($l_{\text{cat}}$) is determined that ensures that the conversion is not complete for a diffusion limited reaction.

Assuming an isothermal parallel plate plug flow reactor, as shown in Fig. 3.8, neglecting axial dispersion and volume changes by the chemical reactions, the local conversion ($X$) is calculated:

$$X = \frac{C_0 - \overline{C}}{C_0}$$  \hspace{1cm} (3.30)

with $\overline{C}$ the average local concentration defined by:

$$\overline{C} = \frac{1}{d_h} \int_0^{d_h} C \, dy$$  \hspace{1cm} (3.31)
The local concentration $C$ between the parallel plates is calculated from the mass balance:

$$v \frac{\partial C}{\partial z} = D_{AB} \frac{\partial^2 C}{\partial y^2}$$

(3.32)

with the boundary conditions:

$$\frac{\partial C}{\partial y} = 0 \quad \text{at} \quad y = 0$$

(3.33)

$$\frac{\partial C}{\partial y} + kC - \frac{C}{D_{AB}} = 0 \quad \text{at} \quad y = d_h$$

(3.34)

$$C = C_0 \quad \text{at} \quad z = 0$$

(3.35)

in which $v$ is the superficial velocity and $k$ is a first order surface reaction rate, e.g. for an adsorption reaction. Equations 3.32 to 3.35 are solved to give [34]:

$$C = 2C_0 \sum_{n=1}^{\infty} e^{-\frac{D_{AB} \alpha_n^2}{v d_h^2}} \frac{(\frac{k^2}{D_{AB}^2} + \alpha_n^2) \cos(\alpha_n y)}{\alpha_n} \sin(\alpha_n d_h)$$

(3.36)

with $\alpha_n$ the positive roots of:

$$\alpha_n \tan(\alpha_n d_h) - \frac{k}{D_{AB}} = 0$$

(3.37)

By substitution of $\frac{k}{D_{AB}}$ for $\alpha_n$, making use of the Damköhler number ($Da = \frac{k d_h}{D_{AB}}$), and the local Graetz number for mass transport ($G_{zm} = \frac{vd_h}{D_{AB}^2}$), the average concentration ($\bar{C}$) across the channel is calculated with Eqs. 3.31 and 3.36 to
give:
\[
\overline{C} = 2C_0 \sum_{n=1}^{\infty} e^{-\frac{\lambda_n^2}{2}} \frac{Da^2}{(Da^2 + Da + \lambda_n^2 \lambda_n^2)}
\]  
(3.38)
in which \(\lambda_n\) are the positive roots of:
\[
\lambda_n \tan(\lambda_n) - Da = 0
\]  
(3.39)
Substitution of Eq. 3.38 into Eq. 3.30, the local conversion (\(X\)) is calculated as:
\[
X = 1 - 2 \sum_{n=1}^{\infty} e^{-\frac{\lambda_n^2}{2}} \frac{Da^2}{(Da^2 + Da + \lambda_n^2 \lambda_n^2)} \lambda_n^2
\]  
(3.40)
In figure 3.9 the local conversion as a function of the inverse Graetz number for various Damköhler numbers is plotted.

![Conversion as a function of the inverse Graetz number for different Damköhler numbers (equation 3.40).](image)

Figure 3.9: Conversion as a function of the inverse Graetz number for different Damköhler numbers (equation 3.40).

Low Damköhler numbers (\(Da \ll 1\)) correspond to a reaction rate limited process, high Damköhler numbers (\(Da \gg 1\)) correspond to a diffusion limited process, like CPO in our reactor. To be able to measure kinetic parameters, the conversion should preferably be considerably less than 100% and therefore the inverse Graetz number is chosen to be \(G_{z^{-1}} = 0.5\), which leads to a catalytic layer length of about 0.008 m. The total length of the channel including the preheating section then becomes 0.02 m. The thermal analysis, discussed in
section 3.2.2.1 shows the temperature gradient over the width of the top wall. At low temperatures, near the side walls of the channel, Rh catalyzes the oxidation of CO and H\textsubscript{2} and decreases the selectivity of the CPO reaction towards synthesis gas. Rh deposition is therefore restricted to the middle of the channel top wall only, to prevent these low temperature oxidation reactions. In practice, the width and length of the sputtered Rh catalyst are controlled using a shadow mask [35].

### 3.2.4 Mechanical design

From the thermal design, it is found that most of the heat provided with the heaters or by the catalytic reaction is lost due to solid heat conduction through the top wall of the channel. It will be clear that the thinner this top wall is made, the less heat is lost. On the other hand, the thinner the top layer the more fragile it becomes. A thin top wall of SiRN or Si\textsubscript{3}N\textsubscript{4} alone would mechanically be unstable at elevated temperatures due to their high thermal expansion coefficients and high intrinsic stress [17]. A mechanical analysis of the channel top wall [23] showed that a composite top wall existing of low stress silicon nitride, introduced for electronic stability, on top of heavily boron doped silicon (p\textsuperscript{++}Si) has an increased flexural rigidity. The flexural rigidity of the top wall is increased by a factor 2.3 when 150 nm of low stress silicon nitride (SiRN), on top of a 850 nm heavily boron doped silicon (p\textsuperscript{++}Si) is used. The shape of the heaters determines the temperature gradient in the top wall and will therefore influence the stress inside the top wall. These stresses are found to be below the yield value and no mechanical instabilities are expected.

### 3.2.5 Electrical design

As stated earlier, the heaters and temperature sensors are situated on top of the thin reaction channel top wall. In this way, the heaters and sensors are in close contact with the catalyst to control the reaction temperature. From the thermal design, Eq. 3.9, it can be found that a heater power of approximately 1.5 W is sufficient to get a temperature of 1100 K at the middle of the channel when \( \varepsilon = 0.3 \). The material chosen for the heaters and sensors is platinum. Platinum has the advantage of a linear temperature resistivity coefficient (\( \alpha \)) up to a temperature of 1120 K [36]. The resistance of a Pt wire as a function of
temperature is given by Eq. 3.41:

\[ R = R_0 (1 + \alpha(T - T_0)) \]  

(3.41)

in which \( R_0 \) is the resistance at room temperature \( T_0 \), and \( R \) is the resistance at temperature \( T \). The value of the linear temperature resistivity coefficient (\( \alpha \)) for Pt thin films appears to deviate from the bulk Pt value. The temperature resistivity coefficient of a thin film heater or sensor will depend on the chemical composition of the film and in case of degradation, of its heating history. At temperatures exceeding 673 K PtO sublimates [33], changing the electrical properties of the heaters and sensors. To prevent the oxidation, the microreactor can be kept in an oxygen free environment. In table 3.3 values for \( \alpha \) found in literature are given, for thin Pt films with a Ti or Ta adhesion layer.

**Table 3.3: Temperature coefficient of resistance (\( \alpha \)) for various Pt film thickness on Ta / SiRN / Si substrates**

<table>
<thead>
<tr>
<th>film composition</th>
<th>( \alpha ) (K(^{-1}))</th>
<th>deposition method</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 nm Pt / 10 nm Ti</td>
<td>0.0029</td>
<td>electron-beam evaporation</td>
<td>[7]</td>
</tr>
<tr>
<td>220 nm Pt / 15 nm Ta</td>
<td>0.0018</td>
<td>CVD</td>
<td>[37]</td>
</tr>
<tr>
<td>270 nm Pt / 15 nm Ta</td>
<td>0.0022</td>
<td>CVD</td>
<td>[37]</td>
</tr>
<tr>
<td>bulk Pt</td>
<td>0.00385</td>
<td>-</td>
<td>[38]</td>
</tr>
</tbody>
</table>

Heater lines can be deposited in different configurations. Using for instance two parallel heater lines will give a more flat temperature profile in the top wall compared to a meandering heater line [9]. However, a meandering line over the width of the channel has the advantage that the temperature at the middle of the channel can be measured at any position along the channel length. In this way, the heater line does not need to be interrupted to position a temperature sensor and a more uniform heating of the top wall is guaranteed. Platinum lines are deposited to serve as resistance temperature sensors. The platinum resistance temperature sensors are positioned in between the meandering heater line. To be able to measure the resistance of these Pt lines, without the resistance of the connection wires, a four-point measurement configuration is used.
3.3 Experimental

3.3.1 Description of the microreactors

With the aid of the above described design considerations, three microreactor prototypes were made. The succeeding generations of microreactors were based on the design issues, developments in the microreactor production process, and experimental experiences obtained with the microreactors. In general the reactors consist of a silicon chip of 1 mm x 30 mm x 45 mm in dimension, see Fig 3.10. On top of the reactor chip heaters and temperature sensors and their electrical connections are deposited. The electrical connection lines end in contact pads at the long sides of the reactor chip to connect the heaters and sensors to a printed circuit board. The heaters and sensors themselves are laying in the middle of the reactor, on top of the reaction channel, as shown in the enlargement in Fig. 3.11(a). The meandering line in the enlargement is a 50 µm wide heater covering 90% of the width of the 500 µm wide reaction channel top wall. The two loops laying in between the meandering heater line are temperature sensors made of 10 µm wide platinum wire. Along the length of the channel, 5 heaters and 12 temperature sensors are positioned. Each heater is 4.1 mm long and has two temperature sensors. At the beginning and at the end of the channel an extra sensor is positioned. The first 3 heaters are used to pre-
Figure 3.11: (a) On the left, a top view of the microreactor-chip (30 mm x 45 mm) is shown with the pattern of the connection wires for the heaters and sensors. Near the long edge of the reactor, the heater and sensor connection wires end in contact pads for electrical connections to a printed circuit board. On the right, an enlargement is shown of the heaters and sensors as used for the first and second reactor prototype. (b) Sketch of the microreactor cross-section. Showing the reaction channel and the thin top wall with the heaters and sensors on top of it and the catalyst on the inside of the channel. The inlet and outlet of the channel are situated in the pyrex bottom plate.
heat the gases to the reaction temperature, the last 2 heaters are used to heat the Rh catalyst. The heaters and sensors are laying on top of a 1-3 µm thin channel top wall as shown schematically in the cross-sectional view in Fig. 3.11(b). This thin top layer allows a good thermal contact between the catalyst beneath it, and the heaters temperature sensors on top of this sheet. The inlet and outlet for the gases are positioned at the bottom of the reaction channel in a Pyrex baseplate. A gas tight sealing is realized, by pressing the reactor chip into a housing equipped with Viton o-rings, see section 3.3.3. The position of the contact pads, the inlet, and outlet are kept the same as well as the dimensions of the complete reactor chip for all reactor prototypes. This enables easy replacement in the set-up.

Three microreactor prototypes have been build and tested, an overview of their characteristic properties, is given in table 3.4.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Prototype I</th>
<th>Prototype II</th>
<th>Prototype III</th>
</tr>
</thead>
<tbody>
<tr>
<td>channel width (µm)</td>
<td>500</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>channel height (µm)</td>
<td>500</td>
<td>500</td>
<td>500</td>
</tr>
<tr>
<td>top wall thickness and composition (µm)</td>
<td>2.7 p++Si(^1) 0.15 SiRN(^2)</td>
<td>0.85 p++Si(^1) 0.15 SiRN(^2)</td>
<td>0.85 p++Si(^1) 0.20 Si(_3)N(_4)</td>
</tr>
<tr>
<td>heaters meandering width (µm)</td>
<td>450</td>
<td>450</td>
<td>150</td>
</tr>
<tr>
<td>maximum operation temperature (K)(^3)</td>
<td>336</td>
<td>630</td>
<td>870</td>
</tr>
<tr>
<td>heater and sensor layout in figure</td>
<td>3.11(a)</td>
<td>3.11(a)</td>
<td>3.12</td>
</tr>
</tbody>
</table>

\(^1\) boron-doped p++ silicon  
\(^2\) silicon rich nitride, low-stress silicon nitride  
\(^3\) maximum temperature see section 3.4.1.2

The differences of the succeeding microreactor prototypes all have the purpose to increase the operation temperature. The second and third prototype have a thinner (1 µm) channel top wall than the first (2.85 µm), to reduce heat loss by conduction and to increase the operation temperature, see section 3.2.2.2. Comparing the second and the third microreactor prototypes, the top wall compo-


3.3.2 Experimental setup

In the experimental setup, schematically shown in Fig. 3.13, the reaction gases are fed by means of mass flow controllers. Oxygen is fed separately from the other reaction gases and mixed with a static mixer just before the reactor inlet. Flames and explosions at the reactor inlet can be prevented by mixing methane or hydrogen with oxygen in a small channel geometry [39]. Catalyst reduction is performed by pretreatment with hydrogen. After the catalyst pretreatment, the hydrogen is exchanged for the reaction mixture by switching two 4-way valves simultaneously. In this way, the reaction feed gases can be analyzed prior to the reaction and the reaction product gases during the reaction with GC (Varian, CP 3800) and MS (Balzers, Thermostar GSD 300 T2).
3.3.3 Microreactor housing

Gas connections to the microreactor chip are made via an aluminium housing, see Fig. 3.14. The housing is designed for easy replacement of the microreactor in case of deterioration or failure.

The electric connections for the heaters and sensors are made with a printed circuit board, see Fig. 3.14. On the printed circuit board springs (IDI SS-30-J-1.3-G) are soldered which press on the contact pads at the end of the sensor and heater lines. The springs are equally distributed along the edge of the chip and therefore press the chip into the housing with a stable and balanced force. The distance between the printed circuit board and the reactor is assured by a H-shape spacer underneath the printed circuit board. In the aluminium housing the chip rests on 12 Viton o-rings (0.74 x 1.02 mm). 2 o-rings are used for the gas seals at the inlet and outlet of the reactor. The other 10 o-rings are used to balance the reactor and prevent it from bending under the force of the springs. After installing a microreactor into the housing, it is tested for gas leakage with the pressure sensor and needle valve downstream of the reactor housing, see Fig. 3.13. At a certain gas flow rate and needle valve position it is verified if there is any leakage by measuring the pressure near the outlet of the reactor. In case of leakage, the pressure is lower than expected.

Most of the heat released by the heaters conducts to the side walls of the channel, see section 3.2.2.2, heating the complete reactor and the reactor housing. First experiments, presented in section 3.4.1.1 showed that the temperature rise of the reactor and the housing is significant. The housing is therefore kept at a constant temperature by means of a oil circulation thermostat (Lauda RM6).
The reactor housing is kept at a temperature of 350 K in this way, water cannot condensate inside the tubing of the microreactor housing and not on the bottom and side walls of the reactor. Good thermal contact between the reactor chip and the aluminium housing is secured by using heat conductive grease between them.

At high temperatures platinum will oxidize in air and at \( T > 673 \text{ K} \) PtO\(_2\) sublimes [33]. The microreactor is placed in a \( \text{N}_2 \) atmosphere, to prevent the platinum oxidation and therefore the sublimation process. In this way, the platinum heater and sensor structures are preserved from oxidation at high temperatures to avoid changes in their electrical resistance.

With a home-made computer interface the electrical power to the heaters is controlled and the resistance of the temperature sensors measured. The poten-
tials and currents of the heaters and the resistances of the sensors are stored with a data acquisition program made in LabVIEW. The heaters are operated in a constant potential mode. In this way the power supplied to the heaters is easier to control. When e.g. the temperature inside the reactor increases because of chemical reactions, the resistance of the heaters will increase. A resistance increase of the heaters results in an electric power decrease \((P = V^2 / R)\) and therefore a temperature decrease. This is in contrast to a constant current controlled system [40] where a disturbance of the temperature is amplified leading to heat-up or cool-down of the reactor. The resistances of the temperature sensors are measured by means of a 4-point measurement. The sensors are operated at a low current (2 mA) to minimize self-heating of the sensors.

3.4 Results and discussion

3.4.1 Thermal experiments

Before experiments could be conducted with the microreactors, the temperature sensors were calibrated. The temperature resistance coefficient is determined with Eq. 3.41 for each temperature sensor by measuring its resistance at different temperatures. In table 3.5 the average temperature resistance coefficient \(\alpha\) of each reactor prototype is shown. These temperature resistance coefficients are all in the same order as the values found in literature, as already shown in table 3.3.

<table>
<thead>
<tr>
<th>prototype</th>
<th>sensor composition</th>
<th>(\alpha) (K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>60 nm Pt</td>
<td>0.0018</td>
</tr>
<tr>
<td>II</td>
<td>200 nm Pt on 10 nm Ta</td>
<td>0.0018</td>
</tr>
<tr>
<td>III</td>
<td>200 nm Pt on 10 nm Ta</td>
<td>0.0021</td>
</tr>
</tbody>
</table>

3.4.1.1 Heat up and cool down experiments

During heating of the first microreactor prototype with the heaters, the temperature of the entire reactor chip and the reactor housing increased due to the heat
conduction from the top wall to the side walls of the channel, see section 3.2.2. The heater/cooler which can keep the reactor and the housing at a stable temperature was not installed at the time the first microreactor was tested. The response of two temperature sensors and the temperature of the microreactor-chip are shown as a function of time in Fig. 3.15(a). At $t = 11$ s the heaters of the reactor are set to 0.5 W, and shutdown again at $t = 158$ s. The temperature measured at sensor 2 is higher as compared to the temperature of sensor 1. This is because sensor 1 is at the beginning of the first heater and sensor 2 at the end of the heater, where the gases flowing through the channel and the top wall of the channel were warmer. The temperature measured with the sensors of the reactor increases over time due to the temperature increase of the reactor chip. Subtracting the temperature of the reactor chip from the sensor readings, the fast temperature response of the channel top wall by turning on and off the heaters is obvious, see Fig. 3.15(b). With Eq. 3.23 it was calculated that the heat-

![Figure 3.15](image_url)

Figure 3.15: (a) The temperature $(T)$ measured with sensor 1, sensor 2, and of the reactor chip as a function of time $(t)$. At $t = 11$ s the heater power is set to 0.5 W. The heater is switched off at $t = 158$ s. (b) The temperature difference $(\Delta T)$ between the measured temperature and the reactor chip temperature as function of time $(t)$ for sensor 1 and 2.

up and cool-down time of the channel top layer is in the order of 2 ms. This
response time is eight times shorter than the time corresponding to the maximum sample frequency of the measurement interface of 60 Hz. Experiments executed by Tiggelaar et al. [23] showed a heat-up and cool-down time in the order of 4 ms. Fast heat-up and cool-down within the millisecond range was validated, giving fast start-up and shut-down of the chemical processes. Fast shut-down of the reactor increases safety in case of failure.

3.4.1.2 Temperature as function of heater power

The temperature sensors are laying on top of the channel wall and measure the temperature of part of the channel top wall. The measured temperature has to be corrected to get the temperature at the catalyst. This correction is achieved with the model, presented in section 3.2.2.1, to calculate the temperature distribution over the width of the channel top wall. With the lateral temperature profile of the channel top wall, the temperature at the sensors and at the catalyst can both be calculated and therefore correlated to each other. The model is validated with experiments, using all reactors. The heaters are set at a specific heating power and the temperature is measured with the sensors of the reactor. In Fig. 3.16 the temperature difference between the microreactor and the average sensor reading is shown as function of the heat supplied by each heater to the top wall. In Fig. 3.16 it can be seen that the modeling results correspond very well with the experiments. The results obtained with Eq. 3.9 and the simulation results with the FEMLAB model presented in section 3.2.2.2 are both valid. The maximum temperature reached at the middle of the top wall and the experimental conditions used are presented in table 3.6. The third microreactor

Table 3.6: Measured and calculated maximum temperatures in the channel top wall

<table>
<thead>
<tr>
<th></th>
<th>Prototype I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>reactor chip temperature (K)</td>
<td>304</td>
<td>351</td>
<td>350</td>
</tr>
<tr>
<td>power on each heater (W)</td>
<td>0.6</td>
<td>1.15</td>
<td>1.3</td>
</tr>
<tr>
<td>measured temperature with the sensors (K)</td>
<td>336</td>
<td>546</td>
<td>615</td>
</tr>
<tr>
<td>calculated temperature at middle of the top wall (K)</td>
<td>347</td>
<td>630</td>
<td>870</td>
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Figure 3.16: Temperature difference ($\Delta T$) between the average temperature measured with the sensors of the reactor ($T$) and the temperature of the reactor chip ($T_s$) as function of the power supplied by each heater ($P$). The solid lines are calculated with Eq. 3.9, the dotted line is calculated with the FEMLAB model presented in section 3.2.2.2. Prototype 1 is the microreactor with a top wall thickness of 2.85 $\mu$m. Prototype 2 is the reactor with a top wall thickness of 1 $\mu$m. Prototype 3 is the microreactor with a top wall thickness of 1.05 $\mu$m and a smaller heater structure.

Prototype started to glow red, dark orange while using a heater power of 1.3 W. The red, dark orange color is an indication for a temperature of 870 - 970 K [41]. Using a heater power of 1.3 W in Eq. 3.9, the temperature in the middle of the top wall is calculated to be 1050 K. The temperature sensors of the reactor, however, indicated 615 K which corresponds to a temperature at the middle of the top wall of 870 K. The large deviation between the calculated and the observed temperatures may originate from deviations in the thermal conductivity of the p++ silicon top wall, which was extrapolated from 350 K in the model equation, but is more likely to be due to heater degradation.
3.4.1.3 High temperature degradation

The temperature resistivity coefficient of the sensors was studied over time to study heater and sensor degradation. A microreactor of the third prototype was heated externally with the heater/cooler of the microreactor housing. The sensors were calibrated up to a temperature of 350 K and the average thermal resistivity coefficient calculated $\alpha = 0.0021 \ K^{-1}$. After this the reactor housing was heated to 425 K and cooled down again to recalibrate the sensors. The resistance at 293 K ($R_0$) of all sensors had increased by an average of 14 % and the thermal resistivity ($\alpha$) had decreased by 33 %. Repeating the heating and recalibration cycle, it is found that $R_0$ of the heaters had now decreased and $\alpha$ had increased. In Fig. 3.17 $R_0$ and $\alpha$ of the sensors are plotted as function of time after each heating and cooling cycle between 293 - 423 K. In Fig. 3.17(a)

\[
R_0 (\Omega) \quad t (h)
\]

\[
\alpha (K^{-1}) \quad t (h)
\]

Figure 3.17: Resistance $R_0$ at 293 K and thermal resistance coefficient $\alpha$ of the 10 sensors after heating and cooling cycles between 293 - 423 K as function of time. (a) Resistance $R_0$ at 293 K as function of time. The lines are drawn through some of the data points as a guide to the eye. (b) The temperature resistivity coefficient $\alpha$ as function of time. The line is drawn through the average values of the 10 sensors.

$R_0$ decreases and increases for each sensor in the same way, therefore it is un-
likely to be caused by errors in the experiments. Next to this, if there was an error in one of the experiments, \( \alpha \) would not change as it is determined from the relative resistance change over temperature, see Eq. 3.41. The temperature resistivity coefficient is a material property, a change in \( \alpha \) over time would indicate that the material has changed. Degradation of the Pt sensor material can be caused by various degradation phenomena like: interlayer diffusion, interlayer reactions as silicidation, stress-induced morphological changes, and surface-diffusion-driven agglomeration (recrystallization). It is found that the effects of these degradation phenomena can be canceled out by first annealing the complete reactor at elevated temperatures, above the normal operation temperature before use [41]. Heating of the second reactor prototype, during catalyst reduction, revealed that the heaters of the microreactor were unreliable. Some heaters failed after 1.5 hours at 530 K, while other heaters could be used at 630 K for 4 hours. In Fig. 3.18 a SEM image is shown of part of the second microreactor prototype top wall. The enlargement shown on the left hand side in Fig. 3.18 is of the middle of the reactor top wall where during operation the temperature has it maximum. Parts of the heating lines have been very warm as melt "droplets", and holes, indicated with arrows, are formed. It is proposed that

Figure 3.18: SEM images of part of the damaged second microreactor prototype [41]. The photo in the middle is an overview of part of the broken top wall, the two images at the sides are enlargements. Due to electrical breakdown of the SiRN layer, the heating line has created a short circuit, and a hot spot is formed. Holes, indicated by arrows and melt "droplets" are the result of these hot spots initiating the rupture of the top wall.
due to electrical breakdown of the SiRN layer a short-circuit between the heater and the electric conducting p++ Si layer has caused the formation of a hot spot. At this hot spot, the thin top wall of the reactor and the heater are damaged, and holes in the top wall are formed. At these perforations, the rupture of the thin channel top wall is initiated by release of the intrinsic tensile stress and by the stresses caused by the temperature gradient at the hot spot. An supplementary study was executed to examine the electrical properties of the SiRN layer [41]. At temperatures above 570 K the SiRN layer losses its insulating properties and electrical breakdown occurs. In the same study Si$_3$N$_4$ layers were also tested for there electrical properties, and it is shown that Si$_3$N$_4$ can be used up to higher temperatures as an electrical insulator. This was also the main reason to built the third microreactor prototype. The third microreactor prototype is equipped with a Si$_3$N$_4$ layer of 200 nm and it is expected to work up to temperatures of 870-920 K with a supply voltage of 15 V on the heaters. In Fig. 3.19 part of the top wall of the third microreactor prototype is shown after heating it for 20 minutes at 870 K with a supply voltage 15 V on the heaters. Comparing the material

Figure 3.19: SEM images of the broken third microreactor top wall. Due to electrical breakdown of the Si$_3$N$_4$ layer, the heating line has created a short circuit, and a hot spot is formed. Holes, indicated by arrows and melt droplets are the result.
damage of the second and third microreactor prototypes, Fig. 3.18 and Fig. 3.19 respectively, the same melt "droplets" and holes can be seen as the result of the electrical breakdown. The top wall of the reactor should be made of SiRN or Si$_3$N$_4$ only to prevent the electrical breakdown. However, a reactor top wall consisting of SiRN or Si$_3$N$_4$ only would mechanically be unstable due to large stresses at high temperatures.

3.4.2 Hydrogen oxidation experiment

The third microreactor failed operation at a maximum temperature of 870 K due to electrical breakdown of the Si$_3$N$_4$ layer. Catalytic partial oxidation of methane cannot be executed at this temperature although it is high enough for catalytic hydrogen oxidation, which is possible at temperatures of 450 K. Hydrogen oxidation was executed in the third reactor prototype to test its safe operation with highly flammable gas mixtures. The rhodium catalyst was reduced by feeding 5 ml min$^{-1}$ hydrogen and 5 ml min$^{-1}$ helium through the reactor while the catalyst was heated to 555 K for 45 min. Hydrogen oxidation was started by feeding a gas mixture of 43 vol% hydrogen and 1.9 vol% oxygen in helium at a flow rate of 12 ml min$^{-1}$. With the mass spectrometer downstream of the reactor, it was verified that the oxygen conversion was 100%.

The hydrogen oxidation reaction is exothermic, the released power from this reaction is 0.325 J s$^{-1}$ for converting 1 ml min$^{-1}$ of O$_2$. Although the used starting gas mixture has an adiabatic temperature rise of 750 K, the temperature rise measured with the reactor was 11 K. Most of the reaction heat conducts through the top wall to the side walls of the channel, consistent with the electrically supplied heat, see section 3.2.2.2.

Flammable mixtures of H$_2$ and O$_2$ were fed to the reactor as is shown in Fig. 3.20. In this figure all used gas concentrations are shown in the flammability diagram of hydrogen, oxygen, and helium. The hatched area shows the flammability region of these three gases at 298 K [42, 43]. Almost all mixtures are flammable at 298 K as can be seen in Fig. 3.20. At the reaction temperature used (> 560 K), the flammability region would extend even further. Figure 3.20 clearly shows that flammable mixtures can be safely processed inside the micro channel. The temperature rise measured at the catalyst due to the heat of reaction is shown
Results and discussion

Figure 3.20: Flammability diagram of hydrogen, oxygen, and helium, the hatched area shows the flammability region at 298 K [42, 43]. The dots inside the ternary diagram show the mole fractions of the hydrogen oxidation experiments realized in microreactor prototype 3.

in Fig. 3.21 as a function of the hydrogen converted. The temperature readings of the sensors upstream and downstream of the catalyst did not change during reaction, and therefore the hydrogen oxidation reaction has only occurred at the catalytic surface and not in the gas phase. The width of the catalyst strip inside the channel is approximately equal to the width of the heaters, see Fig. 3.12. The temperature rise due to the chemical reaction is modeled with Eq. 3.9 by adding the heat of reaction to the applied heater power. The modeling results are plotted in Fig. 3.21 next to the measurements. Although the calculated temperature is close to the measured temperature, it deviates at high hydrogen conversion. This is very likely due to erroneous temperature readings as a result of thermal degradation of the heaters and sensors in time, or current leakage. Prior to the reaction, the reactor was annealed at a temperature of only 470 K which was below the operation temperature of the reactor. Reactor failure occurred after 2
hours and 40 minutes of operation due to water condensation downstream of the reactor.

Figure 3.21: Measured and calculated temperature rise as a function of the amount of hydrogen converted in the hydrogen oxidation experiments.

3.5 Conclusions / outlook

The design of and experiments with a catalytic silicon-based microreactor are presented. The aim of this study was to design a silicon-based microreactor with integrated temperature sensors and heaters for the catalytic partial oxidation of methane. Although the built and tested microreactor was not suitable for CPO of methane, hydrogen oxidation was executed safely.

The microreactor is based on a design with a square reaction channel closed at one side by a thin wall. This thin wall is equipped with heaters and sensors which are in close contact to the catalyst, deposited on the reverse of the thin top wall. The heaters preheat the feed gases and the catalyst to the reaction temperature. Only the thin channel top wall is heated and not the complete reactor chip therefore, gas and electrical connections are easy to make to the reactor. The square reaction channel has a hydraulic diameter of 500 µm and has a preheating section with a length of 0.012 m. After preheating the feed gases, they flow to the reaction section which is 0.008 m long. Inside the reaction section, the reaction will be diffusion limited due to the height of the reaction channel, which was imposed by the production process.
For the microreactor design a model is made of the reactor channel top wall to calculate the temperature profile inside the top wall. With this model, the temperature measured with the sensors of the reactor is predicted. The proposed model was validated by experiments with the different microreactor prototypes. The model could therefore be used to improve the thermal properties of the reactor and to calculate the catalyst temperature from the measured temperatures. With this model it was calculated that most of the heat supplied with the heaters was lost by conduction through the channel top wall. The channel top wall should therefore be as thin as possible for efficient heating. Also reducing the width of the heaters would increase the heating capacity of the reactor as less heat is lost by conduction.

Three microreactor prototypes were built and tested. The three succeeding prototypes were based on design considerations, developments in the production process and experimental experience. The first microreactor could be heated up to temperatures of 336 K. The channel top wall needed to be thinner to reach higher temperatures because most energy supplied by the heaters conducted away through this channel top wall. A thinner top wall was realized in the second microreactor prototype. This microreactor could be heated up to temperatures of 630 K. The maximum temperature of the second reactor prototype was limited due to electrical breakdown of the channel top wall. The reactor top wall consisted of 0.15 µm SiRN and 0.85 µm p+ + Si. The SiRN layer insulates the heaters from the electrically conducting p++Si layer. In a supplementary study [41] it was found that SiRN lost its insulating properties at temperatures above 570 K. In the same study it was found that Si₃N₄ can be used inside the reactor up to temperatures of 870 K before it would start to conduct electricity. In the third microreactor prototype, the 0.15 µm SiRN layer was replaced by an 0.20 µm Si₃N₄ layer. Heating the reactor to a temperature of approximately 870 K makes the heaters glow dark orange. At this temperature, the heaters failed operation after 20 minutes due to electrical breakdown of the Si₃N₄ layer indeed. This makes the reactors not suitable for the catalytic partial oxidation of methane because a reaction temperature up to 1100 K is required. The temperature inside the third microreactor prototype was not high enough for CPO, but suitable for catalytic hydrogen oxidation. Flammable mixtures of hydrogen, oxygen and helium were used at catalyst temperatures between 560 - 670 K.
proving the safe operation of the microreactor. Electrical breakdown of the channel top wall limited the maximum temperature inside the reactor. Leaving out the electrical conducting p++Si layer from the channel top wall would prevent the electrical breakdown but would make the top wall very fragile due to stresses at high temperatures. Making use of corrugated zones to release stress in the heated top wall is a way to overcome this problem which was used in the next reactor prototype, presented in chapter 6.
3.A Convective heat flux

Convective heat flux outside the reactor ($h_o$)

As the top side of the reactor is locally at a higher temperature than the surroundings of the reactor, natural convection can occur because of density differences between the heated gas directly next to the reactor and the surrounding gas. The Rayleigh number ($Ra$) is calculated to determine the heat transfer coefficient by natural convection at the outside of the reactor ($h_o$):

$$Ra = \frac{L' L_0^3 g \rho^2 \beta_{\text{vol}} \Delta T c_{p} H}{\mu^2 \kappa}$$  \hspace{1cm} (3.42)

in which $L'$ is the ratio of the plate surface area to the perimeter, $g$ the gravitational acceleration, $\rho$ the density, and $\beta_{\text{vol}}$ the volumetric thermal expansion coefficient of the fluid, i.e. for an ideal gas $\beta_{\text{vol}} = \frac{1}{T}$. Nusselt correlations ($Nu = \frac{L' h_o}{\kappa}$) are available over a wide range of $Ra$ numbers for heated horizontal plates facing upward:

- $1 < Ra < 200$ \hspace{0.5cm} $Nu = 0.96 Ra^{\frac{1}{4}}$ \hspace{1cm} [44]
- $200 < Ra < 10^4$ \hspace{0.5cm} $Nu = 0.59 Ra^{\frac{1}{4}}$ \hspace{1cm} [44]
- $10^4 < Ra < 10^7$ \hspace{0.5cm} $Nu = 0.54 Ra^{\frac{1}{4}}$ \hspace{1cm} [45]
- $10^7 < Ra < 10^{11}$ \hspace{0.5cm} $Nu = 0.15 Ra^{\frac{1}{4}}$ \hspace{1cm} [45]

For air above the reactor channel top wall ($0.5 \times 30$ mm, $T_i=1100$ K), it is found that $Ra \approx 5.8 \cdot 10^{-3}$ which gives $Nu \approx 1$ as asymptotic value [44]. As $\frac{Nu}{Nu_{\text{con}}}$, heat loss will be caused by conduction only when $Nu = 1$ and therefore $h_o \approx 10$ Wm$^{-2}$K$^{-1}$ [46].

Convective heat flux inside the reactor ($h_i$)

On the inside of the reactor, heat loss from the top wall to the gasses inside the channel will be by forced convection only. Natural convection (Bénard cells) will not occur because the wall with the highest temperature is the top wall of the channel and therefore the direction of gravity is the same as the direction of
the density gradient. The heat transfer coefficient \( (h_i) \) at the inside of the reaction channel topside is calculated by using the Nusselt number at the topside \( (Nu_t) \). In chapter 4, \( Nu_t \) for completely developed flow inside a square channel heated from the topside is determined to be \( Nu_t = 4.69 \) (Eq. 4.8), which gives for the heat transfer coefficient:

\[
h_i = \frac{Nu_t \kappa}{d_h} \approx \frac{4.69 \cdot 0.04}{500 \cdot 10^{-6}} = 375 \frac{W}{m^2K} \tag{3.43}
\]
Appendix

3.B Thermal conductivity

From a mechanical analysis of the reactor top wall it was found that a top wall consisting of 850 nm heavily boron doped silicon \((p^{++}\text{Si})\) and 150 nm SiR\(_N\) or 150 nm Si\(_3\)N\(_4\) layer gives more strength. An overall mean \(\kappa\) of the composite wall is derived, to calculate the temperature profile in this composite top layer (Eq. 3.9). Next to the temperature dependence of \(\kappa\) of the \(p^{++}\text{Si}\), the temperature dependence of \(\kappa\) of the gas phase inside the channel has been considered. Also in this case, a mean value for \(\kappa\) is used.

Composite wall thermal conductivity

The top wall of the channel is made of a layer of 150 nm SiR\(_N\) (\(\delta_{\text{SiR}N}\)) or 200 nm Si\(_3\)N\(_4\) (\(\delta_{\text{Si}_3\text{N}_4}\)) on top of 850 nm \(p^{++}\text{Si}\) (\(\delta_{\text{Si}}\)) for mechanical stability. The thermal conductivity of this composite layer is calculated by taking the weighted average over the thickness of the top wall:

\[
\kappa = \frac{\bar{\kappa}_{\text{Si}}\delta_{\text{Si}} + \kappa_{\text{SiR}N}\delta_{\text{SiR}N}}{\delta_{\text{Si}} + \delta_{\text{SiR}N}}
\]  

(3.44)

in which \(\bar{\kappa}_{\text{Si}}\) equals the mean thermal conductivity of \(p^{++}\text{Si}\) which is considered in the next paragraph. The thermal conductivity of SiR\(_N\) is \(\kappa_{\text{SiR}N} = 3\) W m\(^{-1}\) K\(^{-1}\) [47] and the thermal conductivity of Si\(_3\)N\(_4\) is \(\kappa_{\text{Si}_3\text{N}_4} = 16\) W m\(^{-1}\) K\(^{-1}\) [48].

Thermal conductivity \(p^{++}\text{Si}\)

The thermal conductivity of \(p^{++}\text{-Si}\) top layer of the reaction channel is a strong function of temperature. This dependence should, therefore, be taken into account in the equation for the temperature profile, heat loss, and heat up - cool down calculations given by Eqs. 3.9, 3.11, and 3.23 respectively. The temperature dependency of bulk silicon is shown in Fig. 3.22 [38]. To a good approximation the thermal conductivity of bulk silicon is given by Eq. 3.45

\[
\kappa \approx \kappa_0 \left(\frac{T}{T_0}\right)^m
\]  

(3.45)
Silicon-based microreactor design

in which $\kappa_0$ is the reference thermal conductivity at the reference temperature $T_0$, $\kappa_0 = 119.5 \text{ Wm}^{-1}\text{K}^{-1}$ for bulk Si, $T_0 = 350 \text{ K}$, and $m = -1.198$. The thermal conductivity for $p^{++}$ Si is approximately a factor 1.45 lower than for bulk silicon [23], thus giving for Eq. 3.45: $\kappa_0 = 82.4 \text{ Wm}^{-1}\text{K}^{-1}$ at $T_0 = 350 \text{ K}$.

Within the temperature operation window of the reactor (300 - 1100 K), $\kappa$ varies with a factor of 4.7 in a nonlinear way. Therefore the average thermal conductivity ($\bar{\kappa}$) over the $p^{++}$ Si channel top layer is calculated as:

$$\bar{\kappa} = \int_0^1 \kappa_0 \left( \frac{T_t}{T_0} \right)^m \, d\bar{x}$$  \hspace{1cm} (3.46)

When the heated fraction of the top wall ($\bar{x}$) is small, the temperature profile in the top wall can be approximated by a linear function (Eq. 3.47):

$$T_t \approx T_{\text{max}} - \bar{x}(T_{\text{max}} - T_s)$$  \hspace{1cm} (3.47)

In Fig 3.23 the normalized temperature ($T_t/T_s$), calculated with Eq. 3.9 ($P = 1 \text{ W}, \bar{x} = 0.3$), is plotted together with the linear approximation (Eq.3.47) for half the channel.

By substitution of Eq. 3.47 into Eq. 3.46 and taking $T_0$ equal to $T_s$ the average
The normalized temperature in the top wall \( \left( T_t/T_s \right) \) as a function of the dimensionless position in the top wall \( x \). Only half the channel width is plotted. The solid line is the temperature calculated with Eq. 3.9, the dashed line is the approximation by Eq. 3.47.

\[
\frac{T_t}{T_s} = \frac{T_{\text{max}}}{T_s} - 1 \quad (m + 1)
\]

**Thermal conductivity of gas phase**

The temperature dependence of the thermal conductivity of the gas inside the channel is corrected in the same way as the thermal conductivity of the silicon top wall. Data of N\(_2\) gas [49] were fitted to Eq. 3.45 giving: \( \kappa_0 = 0.0295 \text{ Wm}^{-1} \text{K}^{-1} \) at \( T_0 = 350 \text{ K} \) and \( m = 0.771 \).

### Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_v )</td>
<td>specific surface area</td>
<td>( \text{m}^{-1} )</td>
</tr>
<tr>
<td>( c_p )</td>
<td>heat capacity at constant pressure</td>
<td>( \text{J kg}^{-1} \text{K}^{-1} )</td>
</tr>
<tr>
<td>( C )</td>
<td>concentration</td>
<td>( \text{mol m}^{-3} )</td>
</tr>
<tr>
<td>( d_h )</td>
<td>hydraulic diameter</td>
<td>( \text{m} )</td>
</tr>
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<td>( Da = \frac{k d_h}{D_{AB}} )</td>
<td>Damköhler number</td>
<td>( \text{-} )</td>
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<tr>
<td>( D_{AB} )</td>
<td>diffusion coefficient</td>
<td>( \text{m}^2 \text{s}^{-1} )</td>
</tr>
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<td>( e )</td>
<td>emissivity</td>
<td>( \text{-} )</td>
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<tr>
<td>( g )</td>
<td>gravitation constant,</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( g = 9.81 \text{ ms}^{-2} )</td>
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</table>
\[ G_{zh} = \frac{RePr}{\pi} \] Graetz number for heat transport  
\[ G_{zm} = \frac{\nu \rho}{D_{ABd}} \] Graetz number for mass transport  
\[ h \] heat transfer coefficient  
\[ k \] reaction rate  
\[ Kn \] Knudsen number  
\[ l_H \] length of heater  
\[ L' \] ratio of surface area to the perimeter  
\[ \mathcal{L} \] molecular mean free path  
\[ \dot{n}_h \] specific mass flow rate  
\[ M \] molecular weight  
\[ Nu = \frac{\mathcal{L}d}{\kappa} \] Nusselt number  
\[ P \] power  
\[ Pe = RePr \] Peclet number  
\[ Pr = \frac{\mu c_p}{\kappa} \] Prandtl number  
\[ q \] heat flux  
\[ Q_{\text{con}} \] heat flow rate by conduction  
\[ Q_{\text{for}} \] heat flow rate by forced convection  
\[ Q_{\text{nat}} \] heat flow rate by natural convection  
\[ Q_{\text{rad}} \] heat flow rate by radiation  
\[ R \] temperature ratio defined by Eq. 5.11  
\[ R \] resistance  
\[ R \] gas constant,  
\[ R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \]  
\[ Ra \] Rayleigh number  
\[ Re = \frac{\rho v d_k}{\mu} \] Reynolds number  
\[ t \] time  
\[ T \] temperature  
\[ v \] superficial velocity  
\[ V \] potential  
\[ w_H \] width of heater  
\[ x \] length scale, coordinate  
\[ X \] conversion  
\[ y \] length scale, coordinate  
\[ z \] length scale, coordinate  

**Greek symbols**  
\[ \alpha \] defined by Eq. 3.5  
\[ \alpha \] temperature resistance coefficient  
\[ \alpha \] temperature resistance coefficient (K)
<table>
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<th>Symbol</th>
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<td>( \beta )</td>
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<td>( \beta_{\text{vol}} )</td>
<td>the volumetric thermal expansion coefficient</td>
<td>(K(^{-1}))</td>
</tr>
<tr>
<td>( \delta )</td>
<td>thickness of top wall</td>
<td>(m)</td>
</tr>
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<td>( \varepsilon )</td>
<td>heated fraction of the top wall</td>
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</tr>
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<td>( \theta )</td>
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<td>( \kappa )</td>
<td>thermal conductivity</td>
<td>(W m(^{-1}) K(^{-1}))</td>
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<td>density</td>
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</tr>
<tr>
<td>( \sigma )</td>
<td>Stefan-Boltzmann constant, ( \sigma = 5.67 \cdot 10^{-8} ) W m(^{-2}) K(^{-4})</td>
<td>(W m(^{-2}) K(^{-4}))</td>
</tr>
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<td>diffusion time</td>
<td>(s)</td>
</tr>
<tr>
<td>( \tau )</td>
<td>time constant</td>
<td>(s)</td>
</tr>
</tbody>
</table>

**Subscripts**

- \( g \): gas
- \( h \): heater
- \( i \): inside the channel
- \( \text{in} \): inlet
- \( \text{max} \): maximum
- \( o \): outside the channel
- \( s \): side wall
- \( \text{sb} \): side and bottom wall
- \( t \): top wall
- \( \text{tot} \): total

**References**


Heat and mass transfer in a square microchannel with asymmetric heating

Abstract

This paper describes the heat and mass transfer in a square microchannel that is heated from one side. This microchannel represents a reaction channel in a microreactor that is used to study the kinetics of the catalytic partial oxidation of methane. The microchannel is contained in a silicon wafer and is covered by a thin silicon sheet. At the top side of this sheet, heating elements are present which mimic the heat that is produced as a result of the exothermic chemical reaction. Correlations for Nusselt and Sherwood numbers as a function of the Graetz number are derived for laminar and plug flow conditions. These correlations describe the heat and mass transport at the covering top sheet of the microchannel as well as at its side and bottom walls. By means of computational fluid dynamic simulations, the laminar flow is studied. To determine an approximate laminar flow Nusselt correlation, the heat transport was solved analytically for plug flow conditions to describe the influence of changes in the thermal boundaries of the system. The laminar flow case is experimentally validated by measuring the actual temperature distribution in a 500 µm square, 3 cm long, microchannel that is covered by a 1 µm and by a 1.9 µm thick silicon sheet with heating elements and temperature sensors on top. The Nusselt and Sherwood correlations can be used to readily quantify the heat and mass transport to support kinetic studies of catalytic reactions in this type of microreactor.
4.1 Introduction

Microreactors have characteristic properties, like a high surface to volume ratio, small amounts of chemicals, laminar flow, high heat and mass transfer rates, and short residence times, that make these devices a research topic of high interest. Microstructured chemical reactors are proposed for various applications, such as small-scale production of hydrogen for fuel cells, intrinsic kinetic studies, catalyst screening, and fine-chemicals synthesis [1–3]. The work reported in this paper is part of a project in which a silicon-based microreactor for catalytic partial oxidation of methane to hydrogen and carbon monoxide is developed. This exothermic reaction requires contact times in the order of milliseconds, and therefore a microreactor is very suitable as it typically has short residence times. The microreactor used (Fig. 4.1) is made in silicon at the MESA+ Research Institute.

The reactor has a square reaction channel with a hydraulic diameter of 500 µm and a length of 3 cm. The top wall of the channel is formed by a thin silicon sheet (thickness approximately 1-2 µm). This thin top layer will allow a good thermal contact between the catalyst beneath it, and the 5 heating wires and 12 temperature sensors on top of the sheet. The other three channel walls also consist of silicon. Due to the very high heat conductivity of silicon (148 W m$^{-1}$K$^{-1}$ at 300 K), these three walls will have an equal temperature. As they ensure rapid transfer of heat out of the reaction channel, their temperature will be lower than the mean temperature of the heated top side during steady state operation. The high rate of heat transfer will allow a good control of the reaction conditions inside the channel over a wide range of temperatures [1, 4].

The temperature sensors on top of the channel allow to measure the catalyst temperature accurately, as the distance between the sensors and the catalyst (approximately 1 - 2 µm) is much shorter than the distance between the sensor and the heating wires (45 µm). The heat and mass transport phenomena in the microchannel must be accurately known, to be able to determine the intrinsic kinetics of the catalytic reaction.

The present study focuses on the heat and mass transport inside the square microchannel. By means of computational fluid dynamic (CFD) simulations these transport phenomena can be quantified. However, these calculations are very
Figure 4.1: (a) The left photo is of the microreactor (30 mm x 45 mm); the gray lines are platinum wires. Near the long edge of the reactor, these wires end in pads for connections to a printed circuit board. In the middle of the reactor the platinum wires form five heaters and twelve temperature sensors. The heaters and temperature sensors lie on top of a silicon sheet, covering the reaction channel. The right photo is an enlargement of part of the heater and sensor structures. The thick meandering lines (50 μm wide) are heater elements and the tiny loops (10 μm wide) are two temperature sensors. (b) Schematic representation of a cross-section of the reactor. The inlet and outlet of the square channel are situated on the reverse.
time consuming and are therefore not suitable for general reactor design purposes and kinetic data treatment. For that reason, correlations that describe the dependencies of the Nusselt and Sherwood numbers along the channel axial coordinate are preferred. As the correlations are based on dimensionless numbers, they can also be applied when the dimensions of the square reaction channel change. The Nusselt correlation will be used to calculate the mean gas temperature along the channel and with the Sherwood correlation the mass transport coefficient will be calculated. When the channel diameter is small, rarefaction effects like velocity slip and temperature jump need to be considered \([5–7]\). The channel of our reactor is still large enough (500 µm) to neglect these effects as the Knudsen number \((Kn = 1.6 \cdot 10^{-4}\) for air at 350 K) is less than \(10^{-3}\) and the continuum flow assumption is still valid. Although Nusselt and Sherwood correlations for many different combinations of boundary conditions can be found in literature for square and rectangular (micro)channels \([8–11]\) the specific combination used for our channel were not found. The boundary conditions of the channel are asymmetrical: the boundary condition of the top wall on the one side, and the bottom walls and the side walls of the channel at the other side are different. The heat is produced by an exothermic reaction at the top wall, which will therefore have a higher temperature as compared to the side and bottom walls. Also the mass transport is asymmetrical. The gas components will need to diffuse to the catalytic surface which is only present at the top wall of the channel.

### 4.2 Heat and mass transport in a microchannel

#### 4.2.1 CFD modelling and simulation

To derive the mentioned Nusselt and Sherwood correlations, the specific heat flux \((Q)\) through the microchannel walls as well as the gas temperature distribution \((T_g)\) inside the microchannel is calculated with the CFD package FLUENT 5.5 \([12]\). FLUENT simultaneously solves the momentum, continuity, and energy equations by means of the control volume based technique. The control volumes are defined by means of the computational grid, describing the geometry of the microchannel. In Fig. 4.2 the coordinate system is shown. Because of the symmetry plane at \(x = \frac{1}{2}d\), only half of the geometry is used to make
a computational grid. The grid consists of 12 x 16 x 700 grid points in the (x, y, z) directions. The top wall of the channel is 1 - 2 µm thick (δ) and 3 cm long (L), giving an aspect ratio of 1:15000. This large aspect ratio would give a very dense mesh when the thin silicon sheet is incorporated in it. A dense mesh will result in long calculation time. Therefore the thin top sheet is considered as a heat conducting surface with power generation to take into account the power supplied by the heaters. Because silicon has a high heat conductivity, it is assumed that the temperature of the bottom (T_b) and side walls (T_s) of the microchannel are isothermal. In the simulations nitrogen gas is used as the gas phase with temperature dependent physical properties. In all simulations, the inlet gas temperature is 300 K, the inlet gas velocity is 10 m/s and enters the channel with an uniform velocity profile. At the outlet the pressure is set at 1 atm. Axial dispersion is taken into account in the Fluent simulations although the Peclet number (Pe) is high enough (Pe > 100) to neglect this effect. The flow regime inside the channel is laminar (200 < Re < 500) because of the small diameter of the channel. With the CFD package FLUENT, the heat and mass transport are simulated inside the square microchannel. The laminar flow simulations are compared to the plug flow case in which an uniform distribution of the gas velocity at the cross-section of the channel exists. Analytical solutions for the plug flow case enable us to derive the Nusselt and Sherwood correlations for the laminar flow case.

The FLUENT simulations are verified to ensure the validity of the numerical analysis. The grid dependence of the results is examined by using different mesh sizes. The computational grid used for calculating the presented results gives grid independent results.
4.2.2 Nusselt correlation for laminar flow

With the use of FLUENT simulations, the heat transport at the channel walls is quantified. To be able to calculate the heat transport at the four walls, a subroutine has been written to extract the Nusselt number at a specific coordinate. The Nusselt number at each of the different walls is calculated using Eq. 4.1:

\[
N_u = \frac{Q_i d}{\kappa_i(T_i - T_g)} \quad (4.1)
\]

\( N_u \) is the Nusselt number at wall \( i \), \( Q_i \) the specific heat flux at wall \( i \), \( d \) the hydraulic diameter of the channel, \( \kappa_i \) the thermal conductivity of the gas, \( T_i \) the mean temperature of wall \( i \), and \( T_g \) the bulk mean fluid temperature of the gas. \( Q_i \) and \( T_i \) are calculated as an area weighted average. The Nusselt numbers at all four channel walls are needed to calculate the mean gas temperature inside the channel by means of iteration. From a heat balance over the microchannel it follows:

\[
\dot{m} \left( \frac{dcpT_s}{dz} \right) = N_u t \kappa \frac{a_{v,t}}{d_h}(T_t - T_g) + N_u sb \kappa \frac{a_{v,sh}}{d_h}(T_s - T_g) \quad (4.2)
\]

in which \( \dot{m} \) is specific mass flow rate, \( c_p \) the heat capacity, \( a_{v,t} \) and \( a_{v,sh} \) the specific surface areas of the top wall and of the side and bottom wall respectively, \( N_u t \) the Nusselt number at the top wall, and \( N_u sb \) the average Nusselt number at the side (\( N_u s \)) and bottom (\( N_u b \)) walls (Eq. 4.4). Eq. 4.2 can be written as:

\[
\frac{1}{c_p} \left( \frac{dcpT_s}{dG^{zh}_{2h}} \right) = da_{v,t}N_u t(T_t - T_g) + da_{v,sh}N_u sb(T_s - T_g) \quad (4.3)
\]

in which \( G^{zh}_{2h} \) is the local Graetz number:

\[
G^{zh}_{2h} = Re Pr \frac{d}{z} \quad \text{and} \quad N_u sb = \frac{2N_u s + N_u b}{3} \quad (4.4)
\]

In Fig. 4.3(a) the Nusselt number at the top wall (\( N_u t \)) is plotted against the reciprocal Graetz number. In Fig. 4.3(b) the average Nusselt number at the side and bottom walls (\( N_u sb \)) is plotted against the reciprocal Graetz number.
The temperature of the top wall is changed by varying the power ($P$) on each of the 5 heaters. For the case when all walls are set at an equal temperature, it is found that $N_u = N_{usb} = 2.98$ for $G_{zh}^{-1} > 0.1$ which is in agreement with the literature value [9].

From Fig. 4.3(a) it can be seen that when $T_s = 500$ K and $P = 0.5$ W, the Nusselt number shows a minimum at $G_{zh}^{-1} = 0.05$. This minimum is always found when the inlet temperature of the gas is below the temperature of the side walls. In literature [13], a minimum value for the Nusselt number has also been observed when heat transport is influenced by the wall heat conduction. It is reported that at low $G_{zh}^{-1}$, the Nusselt number approaches the Nusselt number with an isothermal boundary condition. At high $G_{zh}^{-1}$ the Nusselt number approaches the Nusselt number with a constant heat flux boundary condition. In Fig. 4.3, at small $G_{zh}^{-1}$, the $N_u$ and $N_{usb}$ are approximately equal to the
value for the case that all four walls are at the same temperature. At high $Gz_h^{-1}$, the $Nu_t$ and $Nu_{sb}$ are approximately equal to the value for the situation when the side walls have the same temperature as the inlet temperature. To better understand the origin of this transition of $Nu_t$ and $Nu_{sb}$, as the heat transport develops along the reactor length, we solved the equations for plug flow inside the microchannel analytically (appendix 4.A). The transition of the Nusselt number at the top wall we found for the laminar flow case (Fig. 4.3) is also found at plug flow conditions (Fig. 4.7). From Eq. 4.29 it can be seen that the temperature dependence of the Nusselt number in the plug flow case is only determined by the temperature ratio:

$$R = \frac{T_s - T_{in}}{T_t - T_s}$$  \hspace{1cm} (4.5)

The transition of the Nusselt number is similar for laminar and plug flow conditions. At low $Gz_h^{-1}$, the Nusselt number approaches the Nusselt number for $R = \infty$ ($Nu_{R=\infty}$). At high $Gz_h^{-1}$, the Nusselt number equals the Nusselt number for the situation when $R = 0$ ($Nu_{R=0}$), see Fig. 4.3 and 4.7. The transition of the Nusselt number is due to the fact that the heat flux through the side and bottom walls will change direction when the gas inside the channel is heated above the temperature of these walls. This is schematically represented in Fig. 4.4 (a-d).

![Figure 4.4](image)

**Figure 4.4:** Schematic representation of the heat flux direction through the channel walls at different temperatures. The arrows represent the direction of the heat flux through the channel walls.

When the mean temperature of the gas $\overline{T_g}$ is lower than the temperature of the side walls $T_s$, the heat flux is pointing inwards (Fig. 4.4(b)). As soon as the
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mean gas temperature becomes equal to the temperature of the side and bottom walls, there is only a heat flux from the top side (Fig. 4.4(c)). When the mean gas temperature rises further, the heat flux through the side and bottom walls will be pointing outwards (Fig. 4.4(d)). When the heat flux changes direction, $N_{u_{sb}}$ will go to infinity (Fig. 4.3(b)). As soon as the heat flux is reversed (e.g. $G_{z_h}^{-1} = 0.13$ for $R = 2.93$), $N_{u_{sb}}$ is negative and reaches to its asymptotic value at large $G_{z_h}^{-1}$.

To describe the transition of the Nusselt number at the top wall in the laminar flow case, we have used the formulas obtained for the plug flow case. From the plug flow calculations (Eqs. 4.29, 4.31 - 4.38) it can be shown that the Nusselt number for any value of $R$ is described by:

$$\frac{N_u}{N_{u,R=0}} = 1 + \frac{Rq_i}{1 + Rq_i N_{u,R=\infty}} \quad (4.6)$$

in which $N_{u,R=\infty}$, $N_{u,R=0}$, and $q_i$ are all functions of $G_{z_h}^{-1}$. The function $q_i$ is described empirically from the plug flow correlations because the data from the laminar flow CFD simulations gives quite some scattering of the data at low $G_{z_h}^{-1}$. $N_{u,R=0}$ and $N_{u,R=\infty}$ are determined from the laminar flow CFD simulations. The parameters in the empirical equations were estimated by means of non-linear regression, using a Marquardt-Levenberg algorithm implemented in ODRPACK [14]. For the top wall, the empirical equations for $q_i$, $N_{u,R=0}$, and $N_{u,R=\infty}$ are very well approximated by (see Fig. 4.3(a)):

$$q_i = 1 - \tanh (5.9G_{z_h}^{-0.648}) \quad , \quad (4.7)$$

$$N_{u,R=0} = 4.69 \left( 1 + \frac{G_{z_h}}{233} \right)^{0.809} \quad , \quad \text{and} \quad (4.8)$$

$$N_{u,R=\infty} = 2.98 \left( 1 + \frac{G_{z_h}}{181} \right)^{0.906} \quad (4.9)$$

The correlation for the average Nusselt number at the side and bottom walls $N_{u_{sb}}$ is determined in the same way as the Eqs. 4.7 - 4.9. The equations for: $q_{sb}$, $N_{u_{sb},R=0}$, and $N_{u_{sb},R=\infty}$ are empirically determined as:

$$q_{sb} = \frac{0.0545(22.37G_{z_h}^{-0.848})^2}{G_{z_h}^{-1}(1 - \cosh(22.37G_{z_h}^{-0.848}))} \quad , \quad (4.10)$$
\[ N_{ub,R=0} = 0.40 - 1.96 \tanh \left( 7.3G_{zh}^{-0.64} \right) + 5.11 \tanh \left( 17.9G_{zh}^{-0.44} \right), \quad (4.11) \]

\[ N_{ub,R=\infty} = 2.98 \left( 1 + \frac{G_{zh}}{181} \right)^{0.906} \quad (4.12) \]

With the Eqs. 4.10 - 4.12, \( N_{ub} \) can be calculated for any temperature ratio \( R \). In Fig. 4.3(b) it can be seen that the Eqs. 4.10 - 4.12 well describe the \( N_{ub} \) as obtained from the FLUENT simulations. The Nusselt numbers \( N_{ut} \) and \( N_{ub} \) can now be used in Eq. 4.3 to calculate the mean gas temperature.

For both the laminar flow and plug flow cases, the heat flux reversal (Fig. 4.4) is observed when the temperature of the side walls is higher than the inlet temperature and lower than the top wall temperature. Because of this heat flux reversal, the Nusselt number at the top wall will approach its asymptotic value further downstream compared to the cases when there is no heat flux reversal. In Table 4.1 the value of \( G_{zh}^{-1} \) and the corresponding axial position in the microchannel are given at which the Nusselt number has reached 95% of its asymptotic value. For the laminar flow case, the length for 95% development of the heat transfer is longer when there is heat flux reversal \((R \neq 0 \text{ and } R \neq \infty)\) compared to the case when there is no heat flux reversal at the side and bottom walls \((R = 0 \text{ or } R = \infty)\). When \( R = 2.93 \) \((T_s = 500 \text{ K and } P = 0.5 \text{ W})\), \( z_{95\%} \) is even longer than the reactor length and \( N_{ut} \) will not reach 95% of its asymptotic value. In microchannel heat sinks for cooling of electrical devices, a long development length is preferred to get a higher overall heat transport coefficient for a better performance [15]. For kinetic research a high heat transport coefficient and an uniform gas temperature along the reaction channel are

| Table 4.1: Inverse Graetz number and axial position at which the Nusselt number for a different temperature ratio \( R \) has reached 95% of its asymptotic value. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| \( N_{ut} \) \((-)\) | \( G_{zh}^{-1} \) \((-)\) | \( z_{95\%} \) \((\text{mm})\) | \( G_{zh}^{-1} \) \((-)\) | \( z_{95\%} \) \((\text{mm})\) |
| \( N_{ur,R=0} \) | 0.031 | 7 | 0.048 | 11 |
| \( N_{ur,R=\infty} \) | 0.039 | 9 | 0.036 | 8 |
| \( N_{ur,R=2.93} \) | 0.2 | 37 | 0.06 | 13 |
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preferred. When the gas feed temperature is equal to the temperature of the side walls ($R = 0$), the asymptotic value of the $N_{u_t}$ is highest (Fig. 4.3) and the $z_{95\%}$ smallest (Table 4.1).

### 4.2.3 Sherwood correlation for laminar flow

At the top side of the channel, transport of the reactants to the catalyst takes place while the reaction products are transported from the catalyst to the bulk. The reaction rate of the catalytic partial oxidation of methane is very fast and mass transport limitations are likely to occur [16]. When the reaction rate of a component is mass transport limited, the reaction rate will be equal to the mass flux to the catalytic surface:

$$-r = k(C - C_i) \quad (4.13)$$

in which: $r$ is the reaction rate, $k$ the mass transport coefficient, $C$ the species concentration in the bulk, and $C_i$ the concentration at the catalytic surface. The mass transport coefficient is calculated from the Sherwood number. To calculate the Sherwood number at the catalytic surface, the mass transport is determined from a heat transport simulation. With the CFD package FLUENT, heat transport is simulated with the computational grid as discussed in section 4.2.1. As there is no mass transfer at the side and bottom walls, adiabatic boundaries are used. For the catalytic top wall, an isothermal boundary is used as the species concentrations at the catalyst will be constant during stationary operation. From this heat transport calculation, the Nusselt number at the catalytic top wall is calculated using Eq. 4.1. The Nusselt correlation is then converted using the Chilton-Colburn analogy [17–19] to a mass transport correlation, i.e. by substitution of the Sherwood number ($Sh$) for the Nusselt number ($N_{u_t}$), and of the Schmidt number ($Sc$) for the Prandtl number ($Pr$). In Fig. 4.5 the Sherwood number as a function of the inverse Graetz number ($G_{zm}^{-1}$) is shown. The Graetz number is now defined as:

$$G_{zm} = ReSc \frac{d}{z} \quad (4.14)$$

For the mass transport simulations, it is found that $Sh = 2.43$ at $G_{zm}^{-1} > 0.1$, which is in agreement with the literature [20]. $Sh$ as function of $G_{zm}^{-1}$ is very
well approximated by (see Fig. 4.5):

$$Sh = 2.43 \left(1 + \left(\frac{G_z^{-1}}{132}\right)^{0.835}\right)$$

(4.15)

At $G_z^{-1} = 0.08$, the Sherwood number reaches its asymptotic value for 95%. Considering a residence time of 1 ms, the inverse Graetz number of 0.08 corresponds to a length of 18 mm at which the mass transport is 95% developed. For the microreactor used a length of 18 mm corresponds to 60% of the total length. Therefore it is necessary to calculate the Sherwood number as a function of the axial position inside the reactor instead of using a constant value as is done with conventional reactors. With Eq. 4.15 the Sherwood number and therefore the mass transport coefficient can be calculated along the length of the reactor. The mass transport coefficient can be used in Eq. 4.13 to calculate the reaction rate.

### 4.3 Experimental validation

The FLUENT simulations (section 4.2.2) are validated by comparing the calculated temperature at the microchannel top wall with the measured temperature at the top wall.
4.3.1 Microreactor fabrication and connections

The microreactor used for the experiments (see Fig. 4.1) is built at MESA+ Research Institute and is made from silicon wafers using standard silicon-based micromachining technology. To fabricate this reactor, a silicon wafer, polished on both sides, is doped on one side with boron. Afterwards an annealing step is carried out at 1400 K. The annealing step determines the diffusion depth of the boron: the longer the annealing time, the thicker the boron-doped silicon layer and hence the thicker the final top layer covering the reaction channel. After doping and annealing a thin low stress silicon nitride layer is deposited. This layer will insulate the platinum filaments from the silicon substrate. The platinum metal structures (viz. heaters and temperature sensors) are applied using lithography with an image reversal resist, sputtering of the Pt film and lift off in acetone. The flow channel is formed using lithography and three etching steps. First 470 µm deep channels are etched by Deep Reactive Ion Etching (DRIE), followed by wet chemical etching in KOH, and KOH/IPA as etchants. These three etch steps result in a thin top wall of the channel with a high uniformity. A second silicon wafer is used for the bottom wall of the reactor. In this wafer the holes for the gas inlet and outlet of the channel are formed by means of powder blasting. After cleaning both wafers, the reactor is assembled by fusion bonding. The microreactor is mounted to an alumina block with the gas inlet and gas outlet connections. The electrical connections of the heaters and temperature sensors are contacted to a printed circuit board by springs. The current and voltage readings of the heaters and temperature sensors are collected in a data-acquisition system.

4.3.2 Experiments

The FLUENT simulations are validated by measurements, by using the same input parameters for the simulation as the experimental conditions (the power supplied by the heaters, the gas properties, and the gas velocity at the inlet). The temperature sensors on top of the micro channel are calibrated by measuring their resistance while the reactor is heated inside an oven. In Fig. 4.6 the simulated and measured temperature difference between the top wall and the side wall are plotted against the power supplied by the heaters. For the measurements 4 different microreactors are used. The sensor readings
and simulated data are both taken 3.8 mm downstream of the beginning of the heated top wall. To measure the thickness of the channel top wall $\delta$, the reactors are broken and $\delta$ is determined by means of a scanning electron microscope. 1 reactor with a top wall thickness of $\delta = 1.9 \, \mu m$ and 3 reactors with $\delta = 1.0 \, \mu m$ were used for the experiments. From Fig. 4.6 it can be seen that the simulated data correspond very well with the experimental data and the used model is valid. The model can therefore be used to determine the thickness of the channel top layer without breaking the reactor.

4.4 Concluding remarks

In the present study computational fluid dynamic simulations are used to determine the heat and mass transfer characteristics under laminar flow conditions in a square microchannel. The computational fluid dynamic simulations are validated with experiments. From these simulations empirical Nusselt and Sherwood correlations are derived. To describe the heat and mass transport for laminar flow conditions, Nusselt and Sherwood correlations for plug flow conditions are used which are derived from the analytical solution. In Table 4.2 the obtained correlations for laminar flow and plug flow are summarized. These correlations are based on dimensionless numbers (Nusselt, Sherwood, and Graetz number) and can therefore also be used when the dimensions of the square channel change. For both laminar flow and plug flow conditions,
Table 4.2: Nusselt and Sherwood correlations for a square channel heated from the top side (R is the temperature ratio defined by Eq. 4.5).

<table>
<thead>
<tr>
<th>$R$</th>
<th>laminar flow</th>
<th>plug flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$Nu_t = 4.69 \left(1 + \frac{Gzh}{181}\right)^{0.809}$</td>
<td>$Nu_t = 4.597 \left(1 + \left(\frac{Gzh}{181}\right)^{\frac{1}{3}}\right)^{\frac{1}{3}}$</td>
</tr>
<tr>
<td>$\infty$</td>
<td>$Nu_t = 2.98 \left(1 + \frac{Gzh}{181}\right)^{0.906}$</td>
<td>$Nu_t = 4.935 \left(1 + \left(\frac{Gzh}{17.3}\right)^{\frac{1}{3}}\right)^{\frac{1}{3}}$</td>
</tr>
<tr>
<td>all</td>
<td>$Nu_t = Nu_{t,R=0} \frac{1+R_0}{1+R_0 \frac{Nu_{t,R=0}}{Nu_{t,R=\infty}}}$</td>
<td>$Nu_t = Nu_{t,R=0} \frac{1+R_0}{1+R_0 \frac{Nu_{t,R=0}}{Nu_{t,R=\infty}}}$</td>
</tr>
<tr>
<td></td>
<td>$q_t = 1 - \tanh(5.9Gzh)$</td>
<td>$q_t = 1 - \tanh(5.9Gzh)$</td>
</tr>
<tr>
<td>0</td>
<td>$Nu_{sb} = 0.40 - 1.96 \tanh(7.3Gzh^{0.64}) + 5.11 \tanh(17.9Gzh^{0.44})$</td>
<td>$Nu_{sb} = 3.987 - \frac{2}{3} \tanh(6.2Gzh^{0.52}) + 0.445 \tanh(15.6Gzh^{1.27})$</td>
</tr>
<tr>
<td>$\infty$</td>
<td>$Nu_{sb} = 2.98 \left(1 + \frac{Gzh}{181}\right)^{0.906}$</td>
<td>$Nu_{sb} = 4.935 \left(1 + \left(\frac{Gzh}{17.3}\right)^{\frac{1}{3}}\right)^{\frac{1}{3}}$</td>
</tr>
<tr>
<td>all</td>
<td>$Nu_{sb} = Nu_{sb,R=0} \frac{1+R_0}{1+R_0 \frac{Nu_{sb,R=0}}{Nu_{sb,R=\infty}}}$</td>
<td>$Nu_{sb} = Nu_{sb,R=0} \frac{1+R_0}{1+R_0 \frac{Nu_{sb,R=0}}{Nu_{sb,R=\infty}}}$</td>
</tr>
<tr>
<td></td>
<td>$\eta_{sb} = \frac{0.0545(22.37Gzh^{0.84})^2}{Gzh(1-\cosh(22.37Gzh^{0.84}))}$</td>
<td>$\eta_{sb} = \frac{0.0545(22.37Gzh^{0.84})^2}{Gzh(1-\cosh(22.37Gzh^{0.84}))}$</td>
</tr>
<tr>
<td>$Sh_t = 2.43 \left(1 + \left(\frac{Gzh}{132}\right)^{0.835}\right)$</td>
<td>$Sh_t = 2.467 \left(1 + \left(\frac{Gzh}{27.3}\right)^{0.407}\right)$</td>
<td></td>
</tr>
</tbody>
</table>
a heat flux reversal is observed on the side and bottom walls of the channel, when the temperature of the side and bottom walls is higher than the gas inlet temperature. This heat flux reversal is described by the obtained Nusselt correlations. When the inlet gas temperature is equal to the temperature of the side and bottom walls, the asymptotic value of the Nusselt number is the highest. A high Nusselt number results in a high heat transfer coefficient which is preferred for kinetic research. The empirical Nusselt and Sherwood correlations will be used further to model heat and mass transport inside the microreactor to determine reaction kinetic information.
Appendix

4.A Nusselt correlation for plug flow

Heat transport inside a square channel is examined analytically for steady state plug flow conditions with constant gas properties. Although at the top wall of the reactor heat is produced by an exothermic reaction or by the heaters, it is considered as a thermal boundary condition. Due to the high heat conductivity of the silicon the temperature of the top wall is a function of the width of the channel and almost not of the channel length, this is confirmed by the Fluent calculation. The other three walls are assumed to be isothermal. Heat transfer takes place at all four channel walls and as the temperature of the four walls is not the same they are examined separately. The coordinate system used is shown in Figure 4.2. The average Nusselt number at the top wall is defined as [17]:

\[
N_u_t(z) = \frac{\int_0^d \left. \frac{\partial T_g(x,y,z)}{\partial y} \right|_{y=d} \, dx}{\frac{T_t(z) - T_g(z)}{d}}
\]  (4.16)

In Eq 4.16 \(T_g\) is the gas temperature, \(T_t\) is a width weighted average temperature of the top wall at location \(z\), and \(T_g\) is the average gas temperature at location \(z\) which is calculated as the bulk mean fluid temperature over a channel cross section:

\[
T_g(z) = \frac{\int_0^d \int_0^d T_g(x,y,z) \rho v_z c_p \, dxdy}{\int_0^d \int_0^d \rho v_z c_p \, dxdy}
\]  (4.17)

To calculate the gas temperature \(T_g\) inside the square channel from Eqs. 4.16 and 4.17 we have to simultaneously solve the momentum, continuity and energy equations with the boundary conditions. Under the assumption of plug flow (constant gas properties in cross-section perpendicular to z-axis) and neglecting axial thermal conduction, natural convection, viscous dissipation, and internal energy sources, the previous system of equations reduces to the steady state energy equation:

\[
\kappa \left( \frac{\partial^2 T_g(x,y,z)}{\partial x^2} + \frac{\partial^2 T_g(x,y,z)}{\partial y^2} \right) = \rho c_p v_z \frac{\partial T_g(x,y,z)}{\partial z}
\]  (4.18)
To solve this equation, we introduce dimensionless coordinates \( \hat{x} \) and \( \hat{y} \), while \( T_g(x, y, z) \) is replaced by a function \( f(x, y, z) \) (Eq. 4.19) in which \( T_\infty \) is the temperature at an infinite distance downstream of the entrance (\( z = \infty, \frac{\partial T_g}{\partial z} = 0 \)):

\[
\hat{x} = \frac{x}{d}, \quad \hat{y} = \frac{y}{d}, \quad f = \frac{T_\infty(x, y) - T_R(x, y, z)}{T_t - T_s}
\]  

(4.19)

which gives:

\[
\frac{\partial^2 f(x, y, z)}{\partial \hat{x}^2} + \frac{\partial^2 f(x, y, z)}{\partial \hat{y}^2} = \frac{\partial f(x, y, z)}{\partial G z_h^{-1}}
\]  

(4.20)

Eq. 4.20 is solved with the following boundary conditions: \( f = 0 \) at \( \hat{x} = 0 \), \( f = 0 \) at \( \hat{x} = 1 \), \( f = 0 \) at \( \hat{y} = 0 \), and \( f = T_\infty - T_\text{in} \) at \( G z_h^{-1} = 0 \) (reactor inlet), with \( T_\text{in} \) the gas temperature at the inlet. \( T_\infty \) is calculated by solving the heat balance equation on a channel cross-section at \( z = \infty \):

\[
\frac{\partial^2 g(x, y)}{\partial \hat{x}^2} + \frac{\partial^2 g(x, y)}{\partial \hat{y}^2} = 0 \quad \text{with} \quad g(x, y) = \frac{T_\infty(x, y) - T_s}{T_t - T_s}
\]  

(4.21)

The boundary conditions for Eq. 4.21 are: \( g = 0 \) at \( \hat{x} = 0 \), \( g = 0 \) at \( \hat{x} = 1 \), \( g = 0 \) at \( \hat{y} = 0 \), and \( g = (T_\infty - T_\text{in})/(T_t - T_s) \) at \( \hat{y} = 1 \). To solve Eq. 4.21 for the boundary conditions, \( T_\infty \) at \( \hat{y} = 1 \) equals \( T_t \). \( T_t \) is calculated by solving a 1-dimensional heat balance over the width of the thin top sheet:

\[
L \delta \kappa \frac{d^2 T_t}{d \hat{x}^2} + P d - h_o d^2 L(T_t - T_o) - h_i d^2 L(T_t - T_i) = 0
\]  

(4.22)

in which \( h_o \) and \( h_i \) are the heat transfer coefficients outside and inside the reactor respectively, and \( T_o \) and \( T_i \) the gas temperatures outside and inside the reactor respectively (\( T_i = T_g \)). Rewriting Eq. 4.22 gives:

\[
\frac{d^2 T_t}{d \hat{x}^2} - \alpha T_t + \beta = 0
\]  

(4.23)

with:

\[
\alpha = \frac{(h_o + h_i)d^2}{\delta \kappa}, \quad \text{and} \quad \beta = \frac{P d^2}{V_t \kappa} + \frac{h_o d^2 T_o}{\delta \kappa} + \frac{h_i d^2 T_i}{\delta \kappa}
\]  

(4.24)
Nusselt correlation for plug flow

Eq. 4.23 is solved with the boundary conditions \( T = T_s \) at \( \hat{x} = 0 \) and \( T = T_s \) at \( \hat{x} = 1 \) to give the equation for the top wall temperature:

\[
T_t = \frac{\beta}{\alpha} + \left( T_s - \frac{\beta}{\alpha} \right) \frac{\cosh \left( \sqrt{\frac{\alpha}{\beta}} \left( \hat{x} - \frac{1}{2} \right) \right)}{\cosh \left( \sqrt{\frac{\alpha}{\beta}} \frac{1}{2} \right)}
\]  
(4.25)

Eq. 4.25 is well approximated by:

\[
T_t = 6 \left( T_t - T_s \right) \left( \hat{x} - \hat{x}^2 \right) + T_s
\]  
(4.26)

With Eq. 4.26 the boundary conditions for Eq. 4.21 become: \( g = 0 \) at \( \hat{x} = 0 \), \( g = 0 \) at \( \hat{x} = 1 \), \( g = 0 \) at \( \hat{y} = 0 \), and \( g = 6(\hat{x} - \hat{x}^2) \) at \( \hat{y} = 1 \), it follows that:

\[
T_{\infty}(x, y) = T_s + 24(T_t - T_s) \sum_{m=1}^{\infty} \frac{1 - \cos(m\pi)}{m^2\pi^2 \sinh(m\pi)} \sin(m\pi \hat{x}) \sinh(m\pi \hat{y})
\]  
(4.27)

By solving Eq. 4.20 for the function \( f \), the temperature profile inside the channel \( T_{g}(x, y, z) \) can be calculated:

\[
T_{g}(x, y, z) = T_{\infty}(x, y) - (T_t - T_s) \sum_{k=1}^{\infty} \sum_{m=1}^{\infty} \beta_{k,m} \sin(k\pi \hat{x}) \sin(m\pi \hat{y}) \cdot e^{-(k^2 + m^2)\pi^2 G_z h^{-1}}
\]  
(4.28)

with:

\[
\beta_{k,m} = 4 \left( \frac{T_s - T_{in}}{T_t - T_s} (1 - \cos(m\pi)) \right) + \frac{12}{k^2\pi^2} \frac{m^2(-1)^{m+1}}{k^2 + m^2} \frac{1 - \cos(k\pi)}{km\pi^2}
\]  
(4.29)

Substitution of Eq. 4.28 in Eq. 4.17 gives \( T_{g} \). For plug flow calculations \( \rho, v_z, \) and \( c_p \) are constant in a cross section perpendicular to the \( z \)-axis. They are only a
function of $T_g(z)$ and therefore they cancel out of equation 4.17 giving:

$$
T_g(z) = \int_0^1 \int_0^1 T_g(z) \, dx \, dy,
$$

leading to

$$
T_g(z) = T_s + 24(T_l - T_s) \sum_{m=1}^{\infty} \frac{(1 - \cos(m\pi))^2}{m^3 \pi^5},
$$

$$
\frac{1}{\tanh(m\pi)} - \frac{1}{\sinh(m\pi)} - (T_l - T_s),
$$

$$
\sum_{m=1}^{\infty} \sum_{k=1}^{\infty} \beta_{k,m} \frac{1 - \cos(k\pi)}{k\pi} \frac{1 - \cos(m\pi)}{m\pi} e^{-(k^2 + m^2)\pi^2 G_s^{-1}} (4.30)
$$

The Nusselt number at the top wall can now be calculated by substitution of Eqs. 4.28 and 4.30 into Eq. 4.16, giving:

$$
N_{u_t} = \frac{A_t + \sum_{m=1}^{\infty} \sum_{k=1}^{\infty} \beta_{k,m} \frac{m}{k} \cos(m\pi)(1 - \cos(k\pi)) e^{-(k^2 + m^2)\pi^2 G_s^{-1}}}{B_t + \sum_{m=1}^{\infty} \sum_{k=1}^{\infty} \beta_{k,m} \frac{1 - \cos(k\pi)}{k\pi} \frac{1 - \cos(m\pi)}{m\pi} e^{-(k^2 + m^2)\pi^2 G_s^{-1}}} (4.31)
$$

where the constants $A_t$ and $B_t$ follow from:

$$
A_t = 24 \sum_{n=1}^{\infty} \frac{(1 - \cos(n\pi))^2}{n^3 \pi^5 \sinh(n\pi)} \cosh(n\pi) (4.32)
$$

, and

$$
B_t = 1 - 24 \sum_{n=1}^{\infty} \frac{(1 - \cos(n\pi))^2}{n^3 \pi^5 \sinh(n\pi)} (\cosh(n\pi) - 1) (4.33)
$$
Nusselt correlation for plug flow

It follows that \( A_t = 3.26809 \) and \( B_t = 0.71087 \).

The Nusselt number at the side walls is given by:

\[
N_{u_s} = -\frac{1}{T_s - T_g} \left[ \int_0^1 \frac{\partial T_g}{\partial \hat{x}} \bigg|_{\hat{x}=0} \mathrm{d}\hat{y} \right] - A_s + \sum_{m=1}^{\infty} \sum_{k=1}^{\infty} \beta_{k,m} \frac{k}{m} \left( 1 - \cos(k\pi) \right) e^{-\left( k^2 + m^2 \right) \pi^2 G_{z_{\text{h}}}}
\]

\[
N_{u_s} = B_s + \sum_{m=1}^{\infty} \sum_{k=1}^{\infty} \beta_{k,m} \frac{1 - \cos(k\pi) - \cos(m\pi)}{k\pi} e^{-\left( k^2 + m^2 \right) \pi^2 G_{z_{\text{h}}}}\quad (4.34)
\]

with the following constants:

\[
A_s = 24 \sum_{n=1}^{\infty} \frac{\left( 1 - \cos(n\pi) \right)^2}{n^3 \pi^3 \sinh(n\pi)} \left( \cosh(n\pi) - 1 \right) \quad (4.35)
\]

and

\[
B_s = -24 \sum_{n=1}^{\infty} \frac{(1 - \cos(n\pi))^2}{n^3 \pi^3 \sinh(n\pi)} \left( \cosh(n\pi) - 1 \right) \quad (4.36)
\]

After carrying out the summations, it follows that \( A_s = 1.49999 \) and \( B_s = -0.28913 \).

The Nusselt number at the bottom wall is derived from:

\[
N_{u_b} = -\frac{1}{T_b - T_g} \left[ \int_0^1 \frac{\partial T_g}{\partial \hat{y}} \bigg|_{\hat{y}=0} \mathrm{d}\hat{x} \right] - A_b + \sum_{m=1}^{\infty} \sum_{k=1}^{\infty} \beta_{k,m} \frac{m}{k} \left( 1 - \cos(k\pi) \right) e^{-\left( k^2 + m^2 \right) \pi^2 G_{z_{\text{h}}}}
\]

\[
N_{u_b} = B_b + \sum_{m=1}^{\infty} \sum_{k=1}^{\infty} \beta_{k,m} \frac{1 - \cos(k\pi) - \cos(m\pi)}{k\pi} e^{-\left( k^2 + m^2 \right) \pi^2 G_{z_{\text{h}}}}\quad (4.37)
\]

with the constants \( A_b \) and \( B_b \):

\[
A_b = 24 \sum_{n=1}^{\infty} \frac{(1 - \cos(n\pi))^2}{n^3 \pi^3 \sinh(n\pi)} \quad (4.38)
\]
Heat and mass transfer

It is found that $A_b = 0.2681$.

The temperature dependence of the Nusselt number for plug flow is determined by the temperature ratio in Eq. 4.29:

$$R = \frac{T_s - T_m}{T_1 - T_s}$$  \hspace{1cm} (4.39)

By making use of this temperature ratio and the Nusselt numbers at $R = 0$ and $R = \infty$, it can be shown that the Nusselt numbers for any $R$ can be described by:

$$N_{u_t} = N_{u_t, R=0} \frac{1 + Rq_t}{1 + Rq_t} \left( \frac{N_{u_t, R=\infty}}{N_{u_t, R=\infty}} \right)$$  \hspace{1cm} (4.40)

in which $q_t$, $N_{u_t, R=0}$, and $N_{u_t, R=\infty}$ are functions of $Gz_h^{-1}$ which are described empirically for the top wall as:

$$q_t = 1 - \tanh \left( 5.9Gz_h^{-0.647} \right),$$  \hspace{1cm} (4.41)

$$N_{u_t, R=0} = 4.597 \left( 1 + \left( \frac{Gz_h}{63.7} \right)^{\frac{2}{3}} \right)^{\frac{1}{3}},$$  \hspace{1cm} (4.42)

$$N_{u_t, R=\infty} = 4.935 \left( 1 + \left( \frac{Gz_h}{71.3} \right)^{\frac{2}{3}} \right)^{\frac{1}{3}}.$$  \hspace{1cm} (4.43)

The Nusselt numbers for the bottom and side walls are not needed separately (Eq. 4.2), therefore area weighted average of the two is used ($N_{u_{sb}} = \frac{2N_{u_t} + N_{u_b}}{3}$). At $R = \infty$, $N_{u_t} = N_{u_b} = N_{u_{sb}}$. The empirical correlation $q_{sb}$ and $N_{u_{sb}, R=0}$ are determined as:

$$q_{sb} = \frac{0.0545(22.37Gz_h^{-0.848})^2}{Gz_h^{-1}} \left( 1 - \cosh(22.37Gz_h^{-0.848}) \right)$$  \hspace{1cm} (4.44)

$$N_{u_{sb}, R=0} = 3.987 - \frac{2}{3} \tanh(6.2Gz_h^{-0.52}) + 0.445 \tanh(15.6Gz_h^{-1.27})$$  \hspace{1cm} (4.45)

In Figs. A.4.7(a) and A.4.7(b) the Nusselt numbers for the top wall $N_{u_t}$, and the average Nusselt number at the side and bottom walls $N_{u_{sb}}$, are plotted against the inverse Graetz number ($Gz_h^{-1}$). The dots are calculated by the analytical
Figure 4.7: The Nusselt number at the top wall (a) and at the side and bottom wall (b) as a function of the inverse Graetz-number for the square channel with plug flow. For the calculations, an inlet temperature 300 K and an average top wall temperature of 600 K is used. The data points are obtained from Eqs. 4.29 and 4.31 - 4.38. The lines are based on the empirical correlations 4.40 - 4.45.

solution, the lines are the empirical equations. From these Figures it can be seen that the analytical and empirical correlations correspond very well.
Appendix

4.B Sherwood correlation for plug flow

Although we do not need a mass transport correlations for plug flow, we solved it analytically for completeness. Mass transport only takes place at the catalytic top side of the channel. As there is no mass transport taking place through the side walls of the channel, the mass balance does not need to be solved in the x-direction (see Fig. 4.2 for coordinate system used). The mass transport is determined from a heat transport calculation. By making use of the Chilton-Colburn analogy the obtained heat transport correlation is then converted to a mass transport correlation. For the catalytic wall an isothermal boundary is used as the species concentrations will be constant for stationary operation. No mass transport takes place through the bottom wall of the channel. On this wall an adiabatic boundary conditions is used. The Nusselt number at the top wall is calculated by:

\[
Nu_t = \frac{\int_0^1 \frac{\partial T_g}{\partial \tilde{y}} \bigg|_{\tilde{y}=1} \, \tilde{x} \, d\tilde{x}}{T_t - T_{in}} \tag{4.46}
\]

To calculate the gas temperature, the 2-dimensional heat balance over the channel is solved:

\[
\frac{\partial^2 T_g}{\partial \tilde{y}^2} = \frac{\partial T_g}{\partial G z_h^{-1}} \tag{4.47}
\]

The heat balance is solved by replacing the gas temperature \(T_g\) by a dimensionless function \(j\):

\[
j = \frac{T_t - T_g}{T_t - T_{in}} \tag{4.48}
\]

which gives:

\[
\frac{\partial^2 j}{\partial \tilde{y}^2} = \frac{\partial j}{\partial G z_h^{-1}} \tag{4.49}
\]

Eq. 4.49 is solved for the function \(j\) with the following boundary conditions: \(\frac{\partial j}{\partial \tilde{y}} = 0\) at \(\tilde{y} = 0\), \(j = 0\) at \(\tilde{y} = 1\), and \(j = 1\) at \(G z_h^{-1} = 0\), to calculate \(T_g\):

\[
T_g = T_t - (T_t - T_{in}) \frac{4}{\pi} \sum_{n=1}^{\infty} \frac{(-1)^{n+1}}{2n-1} \cos \left( \frac{2n-1}{2} \tilde{y} \right) e^{-\left(\frac{2n-1}{2}\right)^2 G z_h^{-1}} \tag{4.50}
\]
The mean gas temperature $T_g$ at a channel cross section is obtained from:

$$T_g = \int_0^1 T_y \, dy,$$

leading to

$$T_g = T_t + (T_t - T_{in}) \frac{8}{\pi} \sum_{n=1}^{\infty} \frac{1}{(2n - 1)^2} e^{-\left(\frac{2n-1}{2}\pi\right)^2 Gz_m^{-1}}.$$

(4.51)

The Nusselt number at the top wall is calculated by substitution of Eqs. 4.50, 4.51 into 4.46. By using the Chilton Colburn analogy the Sherwood number is obtained:

$$Sh = \frac{\pi^2}{4} \sum_{n=1}^{\infty} \frac{e^{-\left(\frac{2n-1}{2}\pi\right)^2 Gz_m^{-1}}}{\left(\frac{2n-1}{2}\pi\right)^2 Gz_m^{-1}} \left(\frac{Gz_m}{m}\right)^{1/2}.$$  

(4.52)

Eq. 4.52 is approximated by the empirical correlation:

$$Sh = 2.467 \left(1 + \frac{Gz_m}{27.3} \right)^{0.407}.$$  

(4.53)

When $Gz_m^{-1} < 0.001$ Sherwood is proportional to $Gz_m^{0.5}$. In Fig. 4.8 Eqs. 4.52 and 4.53 are plotted.

Figure 4.8: The Sherwood number as a function of the inverse Graetz number for a square channel with plug flow and mass transport only taking place to the top wall of the channel. The data points are obtained from Eq. 4.52 The line is based on the empirical correlation: Eq. 4.53
Appendix

4.C Erratum

The measurements and modeling results presented in Fig. 4.6 were obtained with our best knowledge at the time of publication of the article [21] presented in this chapter. However some small corrections have been made for a more accurate and therefore better representation of the results. The revisions have no influence on the conclusions reported in the article or this chapter. The modifications made and the amended results are given here.

- An improved estimate of the power supplied by the heaters is obtained by also taking the power dissipated in the connection wires on the microreactor into consideration.

- The temperature measured with the sensors was not the average top wall temperature, because the sensors cover 77% of the channel top wall.

- In the model, the thermal conductivity of bulk-silicon is used. However, this should have been the thermal conductivity of p++ silicon which is a factor 1.45 smaller, as described in appendix 3.B.

- The thickness of the silicon top wall of the reaction channel was not 1.9 µm but 2.7 µm. The top wall thickness was measured accurately by first etching a flat surface perpendicular to the top wall surface, followed by SEM measurement.

Due to these modifications in the predicted and measured results of the microreactors the results shown in Fig. 4.6 have changed, the new results are presented in Fig. 4.9. From this figure it can be seen that the modeling results correspond very well with the experimental results and the used model is still valid.
Figure 4.9: The difference between the measured top wall temperature and the side wall temperature as a function of the power supplied by each of the five heaters. The data points are experimental data obtained from measurements with 4 different microreactors, 1 reactor with top wall thickness $\delta = 2.7 \, \mu m$ and 3 reactors with $\delta = 1.0 \, \mu m$ the lines are obtained from FLUENT simulations for different $\delta$. 

$d = 2.7 \, mm$

$T - T_s (K)$

$P (W)$
# Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_v$</td>
<td>specific surface area $(m^2 m^{-3})$</td>
</tr>
<tr>
<td>$A$</td>
<td>constant defined by Eqs. 4.33, 4.36, and 4.38 (-)</td>
</tr>
<tr>
<td>$B$</td>
<td>constant defined by Eqs. 4.33, 4.36, and 4.38 (-)</td>
</tr>
<tr>
<td>$c_p$</td>
<td>heat capacity at constant pressure $(J kg^{-1} K^{-1})$</td>
</tr>
<tr>
<td>$C$</td>
<td>concentration $(mol m^{-3})$</td>
</tr>
<tr>
<td>$d$</td>
<td>side of the square cross-section (m)</td>
</tr>
<tr>
<td>$D_{AB}$</td>
<td>diffusion coefficient $(m^2 s^{-1})$</td>
</tr>
<tr>
<td>$f$</td>
<td>defined by Eq. 4.19 (-)</td>
</tr>
<tr>
<td>$g$</td>
<td>defined by Eq. 4.21 (-)</td>
</tr>
<tr>
<td>$G_{zh} = RePr \frac{d}{2}$</td>
<td>Graetz number for heat transport (-)</td>
</tr>
<tr>
<td>$G_{zm} = ReSc \frac{d}{2}$</td>
<td>Graetz number for mass transport (-)</td>
</tr>
<tr>
<td>$h$</td>
<td>heat transfer coefficient $(W m^{-2} K^{-1})$</td>
</tr>
<tr>
<td>$k$</td>
<td>mass transfer coefficient $(m s^{-1})$</td>
</tr>
<tr>
<td>$Kn$</td>
<td>Knudsen number (-)</td>
</tr>
<tr>
<td>$L$</td>
<td>length of the microchannel (m)</td>
</tr>
<tr>
<td>$\dot{m}$</td>
<td>specific mass flow rate $(kg m^{-2} s^{-1})$</td>
</tr>
<tr>
<td>$N_u = \frac{h d}{\kappa}$</td>
<td>Nusselt number (-)</td>
</tr>
<tr>
<td>$P$</td>
<td>power supplied by the heaters on top of the channel (W)</td>
</tr>
<tr>
<td>$Pe = RePr$</td>
<td>Peclet number (-)</td>
</tr>
<tr>
<td>$Pr = \frac{c_p}{\kappa}$</td>
<td>Prandtl number (-)</td>
</tr>
<tr>
<td>$r$</td>
<td>reaction rate $(mol m^{-2} s^{-1})$</td>
</tr>
<tr>
<td>$R$</td>
<td>temperature ratio defined by Eq. 4.5 (-)</td>
</tr>
<tr>
<td>$Q$</td>
<td>specific heat flux $(W m^{-2})$</td>
</tr>
<tr>
<td>$Re = \frac{\rho v d}{\mu}$</td>
<td>Reynolds number (-)</td>
</tr>
<tr>
<td>$Sc = \frac{\rho D_{AB}}{\mu}$</td>
<td>Schmidt number (-)</td>
</tr>
<tr>
<td>$Sh = \frac{k d}{D_{AB}}$</td>
<td>Sherwood number (-)</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature $(K)$</td>
</tr>
<tr>
<td>$v$</td>
<td>velocity $(m s^{-1})$</td>
</tr>
<tr>
<td>$V$</td>
<td>volume $(m^3)$</td>
</tr>
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<td>$x$</td>
<td>coordinate (m)</td>
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<tr>
<td>$\hat{x} = \frac{x}{d}$</td>
<td>dimensionless coordinate (-)</td>
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<td>$y$</td>
<td>coordinate (m)</td>
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<td>dimensionless coordinate (-)</td>
</tr>
<tr>
<td>$z$</td>
<td>coordinate (m)</td>
</tr>
</tbody>
</table>
Greek symbols

- \( \alpha \) defined by Eq. 4.24 (-)
- \( \beta \) defined by Eq. 4.24 (K)
- \( \delta \) thickness of top wall (m)
- \( \kappa \) thermal conductivity (W m\(^{-1}\) K\(^{-1}\))
- \( \mu \) dynamic viscosity (Pa s)
- \( \rho \) density (kg m\(^{-3}\))

Subscripts

- \( b \) bottom wall
- \( g \) gas
- \( h \) heat transport
- \( i \) inside the channel
- \( in \) inlet
- \( m \) mass transport
- \( o \) outside the channel
- \( s \) side wall
- \( sb \) side and bottom wall
- \( t \) top side
- \( \infty \) at infinite distance downstream of the entrance

References


Abstract

A model is presented to describe the heat and mass transport in a silicon based microreactor for the catalytic partial oxidation (CPO) of methane. The reactor model can be used to assess the reaction kinetics of the CPO reaction. Various aspects of the transport model are examined. The influence of helium and nitrogen as inert gas is studied. It is found that, although the Sherwood number decreases, at fixed axial positions inside the reaction channel, when helium is used as inert, the oxygen conversion during the reaction increases. This increase in conversion is caused by the enhancement of the overall mass transport by increased diffusivity of the reacting species. In the model the Sherwood number changes over the length of the channel. Ignoring this length-dependency would give rise to errors in the kinetics estimation. In the reaction channel a large temperature gradient exists between the catalyst and the opposite channel wall, giving rise to thermal diffusion. However, the influence of thermal diffusion on the conversion and species concentrations near the catalyst are found to be negligible.
5.1 Introduction

Microreactors have become a research topic of high interest due to the characteristic properties they possess. Their small dimensions, in the micrometer range, give them small thermal inertia and a large surface to volume ratio. The small thermal inertia enables the direct control of the reaction conditions [1], whereas their size makes them inherently safe because less chemicals are inside the reactor. The large surface to volume ratio results in short conduction and diffusion pathways for heat and mass transport respectively, therefore these mechanisms are highly improved. Next to these advantages, microreactors are known for their explosion safe operation [2, 3]. As the relatively large surface area tends to remove radical gas species by adsorption, which are crucial for homogeneous gas phase and chain reactions, explosions will be suppressed in micro channels. The reduced explosion danger opens opportunities to study catalytic partial oxidation (CPO) of methane with explosive gas mixtures:

$$2\text{CH}_4 + \text{O}_2 \rightarrow 2\text{CO} + 4\text{H}_2$$

Well known problems in performing kinetic studies on CPO are the temperature measurement at the catalytic surface [4], and mass transport limitations [5]. The heat produced by the exothermic reaction may give rise to hot spot formation and consequently catalyst deactivation. Next to the assessment of catalyst deactivation, catalyst temperature measurements are difficult to perform, as thermocouples often measure the gas phase temperature. Therefore, catalyst temperature measurements are often done by optical detection. The uncertainty in the determination of the catalyst temperature makes it difficult to evaluate the catalytic activity and therefore the reaction mechanism [6].

This work is part of a project in which a silicon-based micro reactor is developed for CPO of methane. The microreactor has a square reaction channel with a hydraulic diameter of 500 µm with heaters and temperature sensors at the top wall, schematically shown in Fig. 5.1(a). The gases enter the reaction channel through the inlet in the bottom wall of the channel. In a preheat section, the inlet gases are heated to a stable temperature before the gases enter the reaction section. In the reaction section, the catalyst is positioned directly underneath the
heated top wall, see Fig. 5.1(b). The temperature of the catalyst can therefore be measured directly as the thin top wall, thickness ca. 1 µm, allows a very good thermal contact between the temperature sensors on top of it and the catalyst inside the channel. A reaction temperature of approximately 1100 K is needed at the catalyst for CPO of methane. The bottom and side walls of the channel are kept at a lower temperature of 373 K to prevent water condensation and to enable a gastight sealing at the in- and outlet of the channel. A more detailed description of the microreactor used is already given in chapter 3.

![Cross-sectional drawing of the reactor](Figure 5.1: (a) Cross-sectional drawing of the reactor. The heaters and temperature sensors lie on top of a thin silicon sheet, covering the reaction channel. The inlet and outlet of the reaction channel are situated on the reverse. (b) Enlargement of part of 2 heaters, 50 µm wide and 2 temperature sensors, 10 µm wide. The photo is taken from the top side of the reactor. Underneath the heater structure, the catalyst is visible as the light gray strip.

CPO of methane is reported to have a very high reaction rate and therefore the reaction rate is likely to be mass transfer limited [5, 7]. Although detailed reactor modeling can be done by means of computational fluid dynamics, the calculation time for these models is exceedingly long and is therefore not convenient to use in kinetic studies. We made a simplified, 2-dimensional model to study the CPO process. The heat and mass transport inside the reactor are calculated using Nusselt and Sherwood correlations. Molecular diffusion of all species to and from the catalyst is taken into account with Stefan-Maxwell diffusion. The microreactor studied has a strong thermal gradient in the order of $1.5 \cdot 10^6$ K/m and thermal diffusion is likely to occur [8]. Thermal or
Soret-diffusion causes small and light molecules to migrate towards hot regions, while large and heavy components move to cold areas. In this chapter, only results are presented. No comparison with experimental data is shown. The model results serve as guidance in designing kinetic CPO experiments. The temperature profile is calculated and a comparison is made for using nitrogen or helium as inert gas. Next to this, the influences of the Sherwood correlation and thermal diffusion on the reaction are examined.

5.2 Reactor transport model

In the reactor model, heat and mass transport phenomena are described locally by Nusselt and Sherwood correlations. In the preheating section the reaction gases are heated to a stable temperature before they enter the reaction section. The Nusselt correlation is used to calculate the radial average gas phase temperature as function of the axial position in the preheat section of the reactor. The average gas phase temperature is needed to calculate the gas phase properties and the dimensionless reactor length of the channel, i.e. the Graetz number for heat transport ($G_z^h$) and mass transport ($G_z^m$). With $G_z^m$ the Sherwood number ($Sh$), and therefore the mass transport coefficient to the catalytic surface, is calculated locally. The mass transport coefficient calculated from the Sherwood correlation is valid for equimolar counter diffusion and is corrected for the non-equimolar counter diffusion to the catalytic surface and for thermal diffusion due to the temperature gradient over the height of the channel. In Fig. 5.2 the complete transport model is shown schematically.

![Figure 5.2: Schematic drawing of the convective heat and mass transport in the reactor sections.](image-url)
5.2.1 Gas phase temperature

The average gas phase temperature \( \overline{T_g} \) is calculated as function of the axial channel coordinate \( z \) with the following heat balance over the channel, as presented in chapter 4 [9]:

\[
\dot{m} \left( \frac{d \overline{T_g}}{dz} \right) = N_{ut} \frac{\kappa c_p}{d_h} (\overline{T_t} - \overline{T_g}) + N_{usb} \frac{\kappa a_{v,t}}{d_h} (T_a - \overline{T_g}) \tag{5.1}
\]

in which \( \dot{m} \) is the specific mass flow rate, \( d_h \) the hydraulic diameter of the channel, \( c_p \) the heat capacity, \( a_{v,t} \) and \( a_{v,sh} \) the specific surface areas of the top wall and of the side and bottom wall, respectively. \( T_t \) is the temperature of the channel side wall and \( T_a \) the average temperature of channel top wall, \( N_{ut} \) the average Nusselt number at the top wall, and \( N_{usb} \) the average Nusselt number at the side and bottom walls. The Nusselt numbers are calculated with the Nusselt correlations Eqs. 5.2 - 5.9, which are taken from chapter 4:

\[
N_{ut,R=0} = 4.69 \left( 1 + \frac{G_{zh}}{233} \right)^{0.809} \tag{5.2}
\]
\[
N_{usb,R=0} = 0.40 - 1.96 \tanh \left( 7.3 G_{zh}^{-0.64} \right) + 5.11 \tanh \left( 17.9 G_{zh}^{-0.44} \right) \tag{5.3}
\]
\[
N_{ut,R=\infty} = 2.98 \left( 1 + \frac{G_{zh}}{181} \right)^{0.906} \tag{5.4}
\]
\[
N_{usb,R=\infty} = 2.98 \left( 1 + \frac{G_{zh}}{181} \right)^{0.906} \tag{5.5}
\]
\[
N_{ut,0 \leq R < \infty} = N_{ut,R=0} \frac{1 + R q_t}{1 + R q_t} N_{usb,R=0} \tag{5.6}
\]
\[
N_{usb,0 \leq R < \infty} = N_{usb,R=0} \frac{1 + R q_{sb}}{1 + R q_{sb}} N_{usb,R=\infty} \tag{5.7}
\]
\[
q_t = 1 - \tanh \left( 5.9 G_{zh}^{-0.648} \right) \tag{5.8}
\]
\[
q_{sb} = \frac{0.0545(22.37 G_{zh}^{-0.848})^2}{G_{zh}^{-1}(1 - \cosh(22.37 G_{zh}^{-0.848}))} \tag{5.9}
\]

These correlations are a function of the Graetz number for heat transport \( (G_{zh}) \) and the side wall temperature ratio \( (R) \). \( G_{zh} \) and \( R \) are defined as:

\[
G_{zh} = Re Pr \frac{d_h}{z} \quad \text{and} \quad R = \frac{T_a - \overline{T_g}}{\overline{T_t} - \overline{T_g}}
\]
in which \( R \) is the Reynolds number, \( Pr \) the Prandtl number, and \( T_{in} \) the gas temperature at the inlet of the channel. The average top wall temperature is calculated by integration of the top wall temperature \( T_t \) derived from chapter 3:

\[
T_t = \int_0^1 T_t \, dx \\
= \frac{A}{\sqrt{\beta}} \sinh(\sqrt{\beta}) + \frac{\alpha + \beta(T_g - T_s)}{\beta} \left( 1 - \frac{1}{\sqrt{\beta}} \sinh(\sqrt{\beta}) \right) \\
+ \frac{\alpha}{\beta \sqrt{\beta}} \sinh \left( \sqrt{\beta} (1 - \varepsilon) \right) - \frac{\alpha}{\beta} (1 - \varepsilon) + T_s
\]

in which \( A \) is defined by Eq. 3.10, \( \alpha \) by Eq. 3.5, \( \beta \) by Eq. 3.6, and \( \varepsilon \) is the heated fraction of the top wall.

### 5.2.2 Mass transport

The radial average gas phase temperature (\( T_g \)), calculated with Eq. 5.1 as function of the reactor length, determines the gas phase properties along the length of the channel and in the reaction section. With the gas phase properties, the Sherwood number (\( Sh \)) and therefore the mass transport coefficient (\( k_{fi}^0 \)) is calculated by making use of the Graetz number for mass transport (\( G_{zm} \)):

\[
G_{zm} = Re \cdot Sc \cdot \frac{d_h}{\delta_b} \quad (5.13)
\]

\[
Sh = 2.43 \left( 1 + \left( \frac{G_{zm}}{132} \right)^{0.835} \right) \quad (5.14)
\]

\[
Sh = \frac{k_{fi}^0 d_h}{D_{im}} = \frac{d_h}{\delta_b} \quad (5.15)
\]

In these equations, \( Sc \) is the Schmidt number, \( D_{im} \) is the diffusion coefficient of component \( i \) in the gas mixture, both at the radial average gas temperature. \( \delta_b \) is the boundary layer thickness. The mass transfer coefficient (\( k_{fi}^0 \)) calculated with the Sherwood number is valid for equimolar counter diffusion. The partial oxidation of methane, \( 2 \text{CH}_4 + \text{O}_2 \rightarrow 2 \text{CO} + 4 \text{H}_2 \), is not equimolar and therefore,
the mass transport coefficient is corrected with the film factor \( y_{fi} \) [10]:

\[
k_{fi} = \frac{k_{0}}{y_{fi}}
\]  

(5.16)

Mass transport is considered in a boundary layer taking into account non-equimolar counter diffusion induced by the heterogeneous reaction and thermal diffusion, to determine the film factor. The film factor is calculated from [10]:

\[
y_{fi} = \frac{(x_{i,b} - x_{i,c})}{\ln \left( \frac{1 + x_{i,b} \frac{\nu_{j}}{\nu_{i}}}{1 + x_{i,c} \frac{\nu_{j}}{\nu_{i}}} \right)}
\]  

(5.17)

with \( N_{g} \) the number of gas components, \( \nu_{i} \) and \( \nu_{j} \) the stoichiometric coefficients of component \( i \) respectively \( j \), and \( x_{i,b} \) and \( x_{i,c} \) the mole fractions of component \( i \) in the bulk and at the catalytic surface, respectively. In the bulk, \( \text{CH}_4 \) and \( \text{O}_2 \) are present. These components will diffuse through the boundary layer and adsorb at the catalytic surface. Mass transport of oxygen to the surface is rate limiting [11, 12] and determines the oxygen concentration at the surface. The concentrations of all components at every position in the boundary layer are calculated with the Stefan-Maxwell diffusion equations including thermal diffusion [13]:

\[
\frac{x_i}{R_g T} \nabla \mu_i = \sum_{j \neq i}^{N_g} \frac{N_j x_j - N_i x_i}{c_{tot} D_{ij}} + \sum_{j \neq i}^{N_g} \left( \frac{D_{ij}^T x_i}{c_{tot} M_j D_{ij}} - \frac{D_{ij}^T x_j}{c_{tot} M_i D_{ij}} \right) \nabla T
\]  

(5.18)

in which, \( R_g \) is the gas constant, \( \mu_i \) the chemical potential of component \( i \), \( N_i \) the molar flux of component \( i \), \( c_{tot} \) the total concentration, \( D_{ij}^T \) the thermal diffusion coefficient of component \( i \), and \( M_i \) the molecular weight of component \( i \).

Equation 5.18 is simplified by assuming ideal gas behaviour:

\[
\frac{x_i}{R_g T} \nabla \mu_i = \nabla x_i
\]  

(5.19)

In addition, Eq. 5.18 is simplified by making use of the thermal diffusion factor \((\alpha_{ij})\), see appendix 5.B. The thermal diffusion factor is related to the thermal
Mass transport limited CPO in microreactor

diffusion ratio \( (k^T_i) \) and is only a weak function of concentration and temperature \([14]\). The thermal diffusion factor and the thermal diffusion ratio express the relative importance of thermal diffusion compared to mass diffusion:

\[
k^T_i = -x_i \sum_{j \neq i}^N x_j \left( \frac{D_j^T}{x_j c_{i\text{tot}} M_{ij} D_{ij}} - \frac{D_i^T}{x_i c_{i\text{tot}} M_{ij} D_{ij}} \right) \tag{5.20}
\]

\[
k^T_i = x_i \sum_{j \neq i}^N x_j \alpha_{ij} \tag{5.21}
\]

Components with a positive \( k^T_i \) move to colder regions, components with a negative \( k^T_i \) move to warmer regions. Furthermore Eq. 5.18 is made dimensionless by using the dimensionless boundary layer thickness:

\[
\hat{y} = \frac{y}{\delta_b} \tag{5.22}
\]

With the above mentioned assumptions, Eq. 5.18 becomes:

\[
\frac{dx_i}{d\hat{y}} = \delta_b \sum_{j \neq i}^N x_i N_j - x_j N_i \frac{c_{i\text{tot}} D_{ij}}{\delta_b x_i} - \delta_b x_i \sum_{j \neq i}^N x_j \alpha_{ij} \frac{d \ln T}{d\hat{y}} \tag{5.23}
\]

In the boundary layer a temperature gradient is present. This can be calculated as follows:

\[
\frac{d}{d\hat{y}} \kappa \left( \frac{dT}{d\hat{y}} \right) = 0 \tag{5.24}
\]

\[
T = \bar{T}_i \quad \text{at} \quad \hat{y} = 0
\]

\[
T = \bar{T}_g \quad \text{at} \quad \hat{y} = 1
\]

with \( \kappa \) the heat conductivity of the gas. The heat conductivity as a function of the temperature \( T \) is calculated with Eq. 5.25, see appendix 5.D:

\[
\kappa = \kappa_0 \left( \frac{T}{T_0} \right)^n \quad \text{with} \quad n \approx 0.76 \tag{5.25}
\]

in which \( \kappa_0 \) is the reference thermal conductivity at the reference temperature \( T_0 \). Integration of Eq. 5.24 over the dimensionless boundary layer thickness \( \hat{y} \).
Reactor transport model

\[ T(\dot{y}) = \frac{1}{A} \left( \frac{T_t}{T_c} \right)^{n+1} \] with \[ A = 1 - \left( \frac{T_g}{T_c} \right)^{n+1} \] (5.26)

and therefore:

\[ \frac{d \ln T}{d \dot{y}} = - \frac{1}{n+1} \frac{A}{1 - \dot{A} \dot{y}} \] (5.27)

The product of the concentration \( c_{\text{tot}} \) and the mass diffusion coefficient \( D_{ij} \) is written as:

\[ c_{\text{tot}} D_{ij} = c_{\text{tot,c}} \left( \frac{T}{T_c} \right) D_{ij,c} \left( \frac{p}{p_t} \right)^m \] with \( m \approx 1.76 \)

\[ = c_{\text{tot,c}} D_{ij,c} (1 - \dot{A} \dot{y})^{m+1} \] with \( n \approx 0.76 \) (5.28)

with \( c_{\text{tot,c}} \) and \( D_{ij,c} \) the concentration and diffusion coefficient at the catalyst temperature \( T_c \). The mass transport of oxygen to the surface limits the reaction rate [11, 12]. The oxygen flux \( N_{O_2} \) to the surface is determined by:

\[ N_{O_2} = c_c x_{1,c} k_{\text{ads}} , \text{ with} \] (5.29)

\[ k_{\text{ads}} = \frac{s}{1 - \frac{s}{2}} \sqrt{\frac{R_g T_c}{2 \pi M}} \] (5.30)

in which \( s = 0.01 \) [11, 15] is the sticking coefficient, \( T_c \) the catalyst temperature, and \( M \) the molecular weight. The ratio of the molar fluxes to the oxygen flux follows from the reaction stoichiometry. The reaction stoichiometry is rewritten, making use of the elements balance, as:

\[ O_2 + FR \cdot CH_4 \rightarrow \frac{2S_{CO}X_{O_2}}{4 - 2S_{H_2} - S_{CO}} CO + \frac{2(1 - S_{CO})X_{O_2}}{4 - 2S_{H_2} - S_{CO}} CO_2 + \frac{4S_{H_2}X_{O_2}}{4 - 2S_{H_2} - S_{CO}} H_2 + \frac{4(1 - S_{H_2})X_{O_2}}{4 - 2S_{H_2} - S_{CO}} H_2O + \left( FR - \frac{2X_{O_2}}{4 - 2S_{H_2} - S_{CO}} \right) CH_4 + (1 - X_{O_2})O_2 \] (5.31)
where \( FR \) is the feed ratio \( F_{\text{CH}_4} : F_{\text{O}_2} \) in the bulk and \( S_{\text{H}_2} \) and \( S_{\text{CO}} \) are the selectivity of respectively hydrogen and carbon monoxide:

\[
S_{\text{H}_2} = \frac{F_{\text{H}_2}}{F_{\text{H}_2} + F_{\text{H}_2\text{O}}} \quad S_{\text{CO}} = \frac{F_{\text{CO}}}{F_{\text{CO}} + F_{\text{CO}_2}}
\]

(5.32)

The molar flux ratios are then given by:

\[
\frac{N_{\text{CH}_4}}{N_{\text{O}_2}} = \nu_{\text{CH}_4} = \frac{2}{4 - 2S_{\text{H}_2} - S_{\text{CO}}}
\]

(5.33)

\[
\frac{N_{\text{H}_2}}{N_{\text{O}_2}} = \nu_{\text{H}_2} = \frac{-4S_{\text{H}_2}}{4 - 2S_{\text{H}_2} - S_{\text{CO}}}
\]

(5.34)

\[
\frac{N_{\text{H}_2\text{O}}}{N_{\text{O}_2}} = \nu_{\text{H}_2\text{O}} = \frac{-4(1 - S_{\text{H}_2})}{4 - 2S_{\text{H}_2} - S_{\text{CO}}}
\]

(5.35)

\[
\frac{N_{\text{CO}}}{N_{\text{O}_2}} = \nu_{\text{CO}} = \frac{-2S_{\text{CO}}}{4 - 2S_{\text{H}_2} - S_{\text{CO}}}
\]

(5.36)

\[
\frac{N_{\text{CO}_2}}{N_{\text{O}_2}} = \nu_{\text{CO}_2} = \frac{-2(1 - S_{\text{CO}})}{4 - 2S_{\text{H}_2} - S_{\text{CO}}}
\]

(5.37)

Substitution of the Eqs. 5.27, 5.28 and 5.33 - 5.37 in Eq. 5.23 gives:

\[
\frac{dx_i}{d\tilde{y}} = \frac{dh N_{\text{O}_2}}{c_{\text{tot},\text{c}}Sh(1 - A\tilde{y})} \left( \frac{\text{mod}}{n+1} \right) \sum_{j \neq i} \frac{x_i \nu_j - x_j \nu_i}{D_{ij,c}} + \frac{dh x_i}{Sh n + 1} \frac{A}{1 - A\tilde{y}} \sum_{j \neq i} x_j \alpha_{ij}
\]

(5.38)

A plug flow model is used to calculate the bulk concentrations, i.e. at the end of the boundary layer, see Eq. 5.39. The flux of the components \((N_i)\) at the catalytic surface equals the flux from the boundary layer to the bulk gas flowing through the reactor:

\[
\frac{dF_i}{d\tilde{V}} = N_i A_c
\]

(5.39)

in which \( F_i \) is the molar flow rate of species i, \( \tilde{V} \) the dimensionless reactor volume \( \tilde{V} = V/V_{\text{tot}} \), and \( A_c \) is the catalytic surface area.

The presented reactor model can be used to assess reaction kinetics of the CPO reaction. The catalyst temperature is measured with the sensors of the reactor. The gas phase temperature and therefore the gas phase properties are calcu-
lated with the heat transport model presented in section 5.2.1. The gas phase properties are used in the mass transport model given in section 5.2.2. In reaction kinetics, the ratios of chemical rate coefficients determine the reaction selectivity and therefore the species fluxes at the catalytic surface. Reaction kinetics of surface reactions can therefore be studied by comparing the measured outlet concentrations of the reactor with calculated results. In this study no CPO measurements were performed with the microreactor, therefore no kinetic studies could be executed and only simulation results are presented in the following.

5.3 Modeling results

In this section, the results of the presented model are given. The calculated gas phase temperature is compared to computational fluid dynamic simulations. The mass transport is examined by comparing the oxygen conversion when He and N\textsubscript{2} are used as inert gas. Next to this, the influence of the Sherwood number and the influence of the thermal diffusion on the oxygen conversion are discussed. As reference reaction conditions for comparison are chosen:

- inlet flow rates (P = 1 atm, T = 373 K):
  - oxygen 10 ml/min, methane 20 ml/min, and nitrogen = 90 ml/min

- temperature:
  - \( T_{\text{in}} = 373 \text{ K}, T_s = 373 \text{ K}, T_c = 1100 \text{ K} \)

- typical values for hydrogen and carbon monoxide selectivities are in the order of [15, 16]:
  - \( S_{\text{H}_2} = 0.8, S_{\text{CO}} = 0.9 \)

- sticking coefficient for oxygen [11, 15]:
  - \( s = 0.01 \)

In the calculations the selectivities to hydrogen and carbon monoxide are set to 0.8 and 0.9 respectively to calculate the flux ratios of the species at the catalytic surface. In a kinetic study the selectivity will, of course, follow from the ratio of the chemical rate coefficients.
5.3.1 Temperature profile in the preheating section

The average gas phase temperature is calculated iteratively from Eq. 5.1 and plotted in Fig. 5.3(a) as function of the channel length coordinate ($z$) for different values of $R$. In Fig. 5.3(a) the data points shown are obtained by computational fluid dynamics (CFD) simulation using FLUENT 5.5 [17]. A detailed description of the CFD model, calculating the laminar convective heat transport inside the square micro channel is given in chapter 4. From Fig. 5.3(a) it can be seen that the approximate calculation of $T_g$ with Eq. 5.1 corresponds very well with the CFD-modeling for different values of $R$. A small discrepancy is shown in Fig. 5.3(a), for the case, that $R = 2.93$ at $z \approx 1$ cm. In all cases with $0 < R < \infty$, $T_g$ will show a discontinuity. For $0 < R < \infty$, heat flux reversal will occur at some place in the reactor as was shown in chapter 4. This discontinuity originates from a non-perfect description of the Nu-number at this point of heat flux reversal. In practice the reactor is used in such a way that $T_{in}$ equals $T_s$, see chapter 3.3.3 and therefore $R = 0$ and no heat flux reversal occurs on the

Figure 5.3: Radial average gas phase temperature $T_g$ as function of the reactor length coordinate ($z$). a) Calculated for different temperature ratios $R$, the solid lines are calculated with Eq. 5.1 and the circles are data points obtained with the FLUENT model described in chapter 4. b) With $R = 0$, $T_{in} = 794$ K, and $T_s = 373$ K.
channel side walls. Taking a heated fraction of the top wall of 0.3, a side wall temperature of 373 K and a catalyst temperature of 1100 K, the average top wall temperature becomes 794 K and the average gas phase temperature, calculated with Eq. 5.1, becomes 503 K. In Fig. 5.3(b) the average gas phase temperature is plotted as function of the reactor length in the reactor preheat section.

5.3.2 Helium versus nitrogen dilution

When helium is used at the same total inlet flow rate as nitrogen, the density of the gas mixture decreases to approximately 32% and therefore the Reynolds number. With nitrogen as inert gas, the Reynolds number at the entrance of the channel is approximately 100. When helium is used instead, the Reynolds number decreases to about 32 at the same residence time. The Sherwood number and therefore the mass transport will develop over a shorter distance inside the reaction channel at a lower Reynolds number, see Fig 5.4(a). The lower mass transport coefficient \( k_{f,0}^{\text{f}} \) at the beginning of the reaction channel decreases the overall conversion. The diffusion coefficients of the reactants in helium compared to nitrogen are approximately three times higher. The higher diffusivity of the components in helium increases the mass transport to the surface and therefore the overall reaction conversion, which counteracts the decrease in Sh. The oxygen conversion \( (X_{O_2}) \) as function of the reaction section length is plotted in Fig. 5.4(b). It can be seen that, as a netto result, the oxygen conversion increases when helium is used instead of nitrogen as the inert. In the examined case, the overall oxygen conversion increases from 48% with nitrogen to 62% with helium as inert gas at \( z = 0.8 \) cm. Using helium instead of nitrogen as inert gas in experiments, the presented transport model can therefore be validated.

5.3.3 Influence of Sherwood correlation

The influence of the Sherwood number on the conversion is already mentioned in section 5.3.2. In the calculations, the Sherwood number, see Fig 5.4(a), and therefore \( k_{f,0}^{\text{f}} \), decreases sharply, especially near the entrance of the reactor. The influence of the developing mass transport over the length of the reactor is examined to see if Eq. 5.14 can be approximated by the constant Sherwood number for fully developed mass transport, \( Sh = 2.43 \). The oxygen conversion as function of the reactor section length is given in Fig. 5.5 for both the Sh-
correlation and the constant value. Near the entrance of the channel, the oxygen conversion increases more rapidly when the Sh-correlation is used instead of the constant Sh-number, as can be seen in Fig. 5.5. The difference in the oxygen conversion, between the Sherwood correlation and the constant value of $Sh = 2.43$, build up near the entrance, explains the difference of $\approx 4\%$ near the exit of the reactor. The overall oxygen conversion at the reactor exit is approximately the same when $Sh = 3$ is used instead of the Sherwood correlation. The oxygen conversion calculated with $Sh = 3$, catches up with the lower Sherwood number of the developing Sherwood correlation. Equation 5.14 should therefore not be replaced by a constant value in kinetic research as the conversion along the length of the reactor would be inaccurate.

5.3.4 Influence of thermal diffusion

Inside the reaction channel a temperature gradient is present between the heated top wall and the side and bottom walls of the channel. The high temperature gradient of $\approx 1.5 \cdot 10^6$ K/m, will cause mass transport by thermal diffusion over
Figure 5.5: Oxygen conversion as function of the length of the reaction section. The solid line is calculated with the Sherwood correlation, Eq. 5.14, the dashed line with Sh = 2.43, and the dotted line with Sh = 3.

the height of the channel. The relative importance of thermal diffusion to mass diffusion is studied with the thermal diffusion ratio \( (k_i^T) \), see Eq. 5.20. The thermal diffusion ratios for oxygen \( (k_{O_2}^T) \) and hydrogen \( (k_{H_2}^T) \) are plotted in Fig. 5.6 as function of the reactor length and for 75 vol% nitrogen and helium dilution, with the same total inlet flow rate. The thermal diffusion ratio is in the order of -0.03 to 0.03 for oxygen and hydrogen in nitrogen or helium dilution, as can be seen from Fig. 5.6. Hydrogen diffusion is influenced most when nitrogen is used as an inert gas near the exit because of its highest concentration at the exit and due to the mass difference between these components. When helium is used as inert gas, thermal diffusion has less effect on the hydrogen diffusion because hydrogen and helium have about the same molecular mass. At higher concentrations the influence of thermal diffusion on the concentration gradient increases, e.g. 33 vol% O\(_2\) and 66.6 vol% CH\(_4\) in the feed gases give \( k_{H_2}^T \approx -0.07 \) at the exit of the channel. The influence of thermal diffusion on the diffusion processes is about 7%. In order to calculate the influence of thermal diffusion on the conversion, the thermal diffusion factor \( (\alpha_{i,j}) \) is made equal to zero to cancel out the effects of thermal diffusion. From modeling results it is found that thermal diffusion has no influence on the calculated conversion and almost no influence, i.e. <0.01%, on the species concentration at the catalytic surface. Therefore thermal diffusion effects can be neglected in a kinetic study.
Figure 5.6: Thermal diffusion ratio ($k_{ij}^T$) for oxygen and hydrogen as function of the reaction section length ($z$). The solid lines are for nitrogen as inert gas, the dashed lines are for helium as inert gas, both 75 vol% in the feed gas.

of CPO in this type of reactor.

5.4 Conclusions

A model is presented to describe the mass and heat transport inside a square micro reaction channel. The model can be used to determine reaction kinetic information from the mass transport limited catalytic partial oxidation of methane. Nusselt correlations are used to calculate the average gas phase temperature inside the channel and the results are validated by computational fluid dynamic simulations.

The catalytic partial oxidation of methane is known to be strongly mass transport limited and mass transport will therefore determine the conversion. However, selectivity issues are not determined by mass transport but by reaction kinetics at the catalytic surface. Using helium instead of nitrogen as an inert gas, the mass transport to and from the catalytic surface is changed because the physical properties of the gas change. When helium is used, the density of the gas mixture and therefore the Reynolds number decrease with a factor 3. The lower Reynolds number results in a lower local Sherwood number. Despite the lower Sherwood number, the oxygen conversion increases with 14% as the
diffusion coefficients of all components increase by a factor of about 3 when helium is used.

The influence of the developing Sherwood number along the reaction channel length on the oxygen conversion is examined by comparing it with constant Sherwood numbers of 2.43 and 3. The high Sherwood number at the entrance of the channel builds up a difference in oxygen conversion of approximately 4% compared to a constant Sherwood number of 2.43. Using a constant Sherwood number of 3 the same conversion as with the developing Sherwood correlation is reached at the reactor exit. However, this is not suitable for kinetic research as the choice of a constant Sherwood number influences the oxygen concentration and therefore its conversion along the length of the reactor.

Thermal diffusion was taken into account in the modeling results because a temperature gradient of about $1.5 \cdot 10^6$ K/m exists inside the reaction channel. It is found that thermal diffusion has almost no effect on the conversion and changes the species concentrations at the catalytic surface by 0.01% at most. Thermal diffusion can therefore be neglected in the mass transport model.
Appendix

5.A Mass diffusion coefficients

The binary mass diffusion coefficients $D_{ij}$ are calculated with [18, 19]:

$$D_{ij} = \frac{1.858 \cdot 10^{-7} T^{3/2} \left( \frac{1}{M_i} + \frac{1}{M_j} \right)^{1/2}}{P \sigma_{ij}^2 \Omega_D}$$

(5.40)

with $P$ the pressure, $\sigma_{ij}$ the collision diameter defined by Eq. 5.41 and table 5.1, and $\Omega_D$ the collision integral for molecular diffusion defined by Eq. 5.42 [20].

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$$

(5.41)

$\Omega_D$ is calculated from [20]:

$$\Omega_D = \frac{A}{\left( \frac{\kappa T}{\varepsilon_{AB}} \right)^B} + \frac{C}{\exp \left( \frac{\kappa T}{\varepsilon_{AB}} D \right)} + \frac{E}{\exp \left( \frac{\kappa T}{\varepsilon_{AB}} F \right)} + \frac{G}{\exp \left( \frac{\kappa T}{\varepsilon_{AB}} H \right)}$$

(5.42)

\[
\begin{align*}
A &= 1.06036 & D &= 0.47635 & G &= 1.76474 \\
B &= 0.15610 & E &= 1.03587 & H &= 3.89411 \\
C &= 0.19300 & F &= 1.52996 \\
\end{align*}
\]

$$\frac{\varepsilon_{AB}}{\kappa} = \sqrt{\frac{\varepsilon_A \varepsilon_B}{\kappa \kappa}}$$

(5.43)

Equation 5.42 is a function of temperature, this function is approximately proportional to:

$$\Omega_D \propto T^{-0.26}$$

(5.44)

The effect of temperature on the mass diffusion coefficient is therefore proportional to:

$$D_{ij} \propto T^{1.76}$$

(5.45)
Thermal diffusion factor

Table 5.1: Lennard-Jones parameters and collision diameters of different components [18]

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\varepsilon_1/\kappa$ (K)</th>
<th>$\sigma$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>carbon dioxide</td>
<td>190</td>
<td>3.996</td>
</tr>
<tr>
<td>carbon monoxide</td>
<td>110</td>
<td>3.590</td>
</tr>
<tr>
<td>helium</td>
<td>10.22</td>
<td>2.576</td>
</tr>
<tr>
<td>hydrogen</td>
<td>33.3</td>
<td>2.968</td>
</tr>
<tr>
<td>methane</td>
<td>136.5</td>
<td>3.822</td>
</tr>
<tr>
<td>nitrogen</td>
<td>91.5</td>
<td>3.681</td>
</tr>
<tr>
<td>oxygen</td>
<td>113</td>
<td>3.433</td>
</tr>
<tr>
<td>water</td>
<td>356</td>
<td>2.649</td>
</tr>
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Appendix

5.B Thermal diffusion factor

Thermal diffusion factors of the used components are given in table 5.2.

Table 5.2: Thermal diffusion factors ($\alpha_{ij}$) [14]

<table>
<thead>
<tr>
<th>trace ↓</th>
<th>Carrier →</th>
<th>CH$_4$</th>
<th>O$_2$</th>
<th>H$_2$</th>
<th>H$_2$O</th>
<th>CO</th>
<th>CO$_2$</th>
<th>N$_2$</th>
<th>He</th>
</tr>
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<tbody>
<tr>
<td>CH$_4$</td>
<td></td>
<td>0</td>
<td>-0.08</td>
<td>0.44</td>
<td>-0.03</td>
<td>-0.07</td>
<td>-0.16</td>
<td>-0.07</td>
<td>0.48</td>
</tr>
<tr>
<td>O$_2$</td>
<td>0.09</td>
<td>0</td>
<td>0.44</td>
<td>0.08</td>
<td>0.02</td>
<td>-0.09</td>
<td>0.02</td>
<td>0.52</td>
<td></td>
</tr>
<tr>
<td>H$_2$</td>
<td>-0.30</td>
<td>-0.29</td>
<td>0</td>
<td>-0.39</td>
<td>-0.29</td>
<td>-0.35</td>
<td>-0.29</td>
<td>-0.05</td>
<td></td>
</tr>
<tr>
<td>H$_2$O</td>
<td>0.03</td>
<td>-0.04</td>
<td>0.36</td>
<td>0</td>
<td>-0.03</td>
<td>-0.10</td>
<td>-0.02</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>0.07</td>
<td>-0.02</td>
<td>0.45</td>
<td>0.07</td>
<td>0</td>
<td>-0.11</td>
<td>0</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0.18</td>
<td>0.10</td>
<td>0.55</td>
<td>0.21</td>
<td>0.12</td>
<td>0</td>
<td>0.12</td>
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<tr>
<td>N$_2$</td>
<td>0.07</td>
<td>-0.02</td>
<td>0.45</td>
<td>0.07</td>
<td>0</td>
<td>-0.11</td>
<td>0</td>
<td>0.53</td>
<td></td>
</tr>
<tr>
<td>He</td>
<td>-0.33</td>
<td>-0.34</td>
<td>0.05</td>
<td>-0.43</td>
<td>-0.34</td>
<td>-0.42</td>
<td>-0.33</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
Appendix

5.C Viscosity

The gas viscosity can be defined via the kinetic theory as:

\[ \mu = 2.669 \cdot 10^{-6} \sqrt{\frac{TM}{\sigma^2 \Omega_\mu}} \]  \hspace{1cm} (5.46) 

In which \( \Omega_\mu \) is the collision integral for molecular viscosity which can be calculated with \[20\]:

\[ \Omega_\mu = A \left( \frac{\kappa T}{\varepsilon} \right)^{-B} + C \exp \left( -\frac{\kappa T}{\varepsilon} D \right) + E \exp \left( -\frac{\kappa T}{\varepsilon} F \right) \]  \hspace{1cm} (5.47) 

\[ A = 1.16145 \quad C = 0.52487 \quad E = 2.16178 \]
\[ B = 0.14874 \quad D = 0.77320 \quad F = 2.43787 \]

Equation 5.47 is approximately proportional to:

\[ \Omega_\mu \propto T^{-0.26} \]  \hspace{1cm} (5.48) 

Therefore the viscosity as a function of temperature is proportional to:

\[ \mu \propto T^{0.76} \]  \hspace{1cm} (5.49) 

Appendix

5.D Thermal conductivity

For a gas the thermal conductivity can be calculated using the modified Eucken relation \[20\]:

\[ \kappa = 1.15 \frac{\mu (c_p - R_g)}{M} + 2.03 \frac{\mu R_g}{M} \]  \hspace{1cm} (5.50) 

As \( c_p \) is a minor function of temperature compared to \( \mu \), from equation 5.49 it can be seen that:

\[ \kappa \propto T^{0.76} \]  \hspace{1cm} (5.51)
Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_v$</td>
<td>specific surface area</td>
<td>(m$^{-1}$)</td>
</tr>
<tr>
<td>$A_c$</td>
<td>catalytic surface</td>
<td>(m$^2$)</td>
</tr>
<tr>
<td>$c_p$</td>
<td>heat capacity at constant pressure</td>
<td>(J kg$^{-1}$ K$^{-1}$)</td>
</tr>
<tr>
<td>$c$</td>
<td>concentration</td>
<td>(mol m$^{-3}$)</td>
</tr>
<tr>
<td>$d_h$</td>
<td>hydraulic diameter</td>
<td>(m)</td>
</tr>
<tr>
<td>$D_{ij}$</td>
<td>binary mass diffusion coefficient</td>
<td>(m$^2$ s$^{-1}$)</td>
</tr>
<tr>
<td>$D_i$</td>
<td>thermal diffusion coefficient</td>
<td>(kg m$^{-1}$ s$^{-1}$)</td>
</tr>
<tr>
<td>$F_i$</td>
<td>molar flow rate of species i</td>
<td>(mol s$^{-1}$)</td>
</tr>
<tr>
<td>$G_{zh}$</td>
<td>Graetz number for heat transport</td>
<td>(-)</td>
</tr>
<tr>
<td>$G_{zm}$</td>
<td>Graetz number for mass transport</td>
<td>(-)</td>
</tr>
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<td>$k_i$</td>
<td>thermal diffusion ratio</td>
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</tr>
<tr>
<td>$l$</td>
<td>length of the microchannel</td>
<td>(m)</td>
</tr>
<tr>
<td>$m$</td>
<td>specific mass flow rate</td>
<td>(kg m$^{-2}$ s$^{-1}$)</td>
</tr>
<tr>
<td>$N_i$</td>
<td>molar flux</td>
<td>(mol m$^{-2}$ s$^{-1}$)</td>
</tr>
<tr>
<td>$N_u$</td>
<td>Nusselt number</td>
<td>(-)</td>
</tr>
<tr>
<td>$Pr$</td>
<td>Prandtl number</td>
<td>(-)</td>
</tr>
<tr>
<td>$R$</td>
<td>gas constant, temperature ratio defined by Eq. 5.11</td>
<td>(-)</td>
</tr>
<tr>
<td>$Re$</td>
<td>Reynolds number</td>
<td>(-)</td>
</tr>
<tr>
<td>$s$</td>
<td>sticking coefficient</td>
<td>(-)</td>
</tr>
<tr>
<td>$Sc$</td>
<td>Schmidt number</td>
<td>(-)</td>
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<tr>
<td>$Sh$</td>
<td>Sherwood number</td>
<td>(-)</td>
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<tr>
<td>$T$</td>
<td>temperature</td>
<td>(K)</td>
</tr>
<tr>
<td>$V$</td>
<td>volume</td>
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<td>mole fraction</td>
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<td>$y$</td>
<td>length scale, coordinate</td>
<td>(m)</td>
</tr>
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<td>$y_i$</td>
<td>dimensionless coordinate</td>
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</tr>
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<td>$y_f$</td>
<td>film factor</td>
<td>(-)</td>
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<tr>
<td>$z$</td>
<td>length scale, coordinate</td>
<td>(m)</td>
</tr>
<tr>
<td>$\hat{z}$</td>
<td>dimensionless coordinate</td>
<td>(-)</td>
</tr>
</tbody>
</table>

Greek symbols
Mass transport limited CPO in microreactor

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>α_{ij}</td>
<td>thermal diffusion factor</td>
<td>(-)</td>
</tr>
<tr>
<td>δ_{ib}</td>
<td>boundary layer thickness</td>
<td>(m)</td>
</tr>
<tr>
<td>κ</td>
<td>thermal conductivity</td>
<td>(W m^{-1}K^{-1})</td>
</tr>
<tr>
<td>μ</td>
<td>viscosity</td>
<td>(Pa s)</td>
</tr>
<tr>
<td>μ_ν</td>
<td>chemical potential</td>
<td>(J mol^{-1})</td>
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<tr>
<td>σ_{ij}</td>
<td>collision diameter</td>
<td>(Å)</td>
</tr>
<tr>
<td>Ω_D</td>
<td>collision integral for molecular diffusion</td>
<td>(-)</td>
</tr>
<tr>
<td>Ω_{μ}</td>
<td>collision integral for molecular viscosity</td>
<td>(-)</td>
</tr>
</tbody>
</table>

**Subscripts**

- 0: reference
- b: bulk
- c: catalyst
- g: gas
- h: heat transport
- i: component i
- in: inlet
- m: mass transport, mixture
- o: outside the channel
- s: side wall
- sb: side and bottom wall
- t: top wall
- tot: total

**References**


References


Abstract

A silicon-based microreactor for high temperature catalytic gas reactions is designed and tested in this chapter. The reactor design is based on a previous reactor design which suffered from electrical breakdown at elevated temperatures. In the new reactor, electrical breakdown is prevented by making use of heaters which are suspended in low stress silicon nitride tubes. The suspended tubes function as a corrugated layer to release thermally induced stresses in the silicon nitride layer. The microreactor is operated for 110 hours at approximately 900 K without failure and stable heater performance. Operation temperatures above 1000 K are reached with the suspended heater reactor, which makes it suitable for reaction kinetic research of catalytic partial oxidation reactions.
6.1 Introduction

This chapter is part of a feasibility study to build and operate a silicon based microreactor for the catalytic partial oxidation of methane. Microreactors offer small length scales which enhance heat and mass transport and will therefore enhance heat or mass transport limited reaction rates. Partial oxidation reactions have short reaction times and are often constrained by heat and mass transport [1]. This makes these reactions very suitable for microreactor applications. The aim is to develop a microreactor, which can be utilized as a research tool to study the reaction kinetics of the catalytic partial oxidation (CPO) of methane. Catalytic partial oxidation of methane can be executed with high conversion and selectivity at a temperature of 1100 K [2] over a rhodium catalyst. Microreactors, which are to be used for high temperature reactions like CPO, will not only have to resist high temperatures, but also high thermal gradients, because of their small length scales. These large temperature gradients give rise to thermally induced mechanical stress, which can become destructive.

In chapter 3 we described the design of and experiments with a microreactor, which could be operated up to 870 K. This microreactor consists of a 30 mm long square reaction channel with a hydraulic diameter of 500 μm. The square channel is closed at the top by a 1 μm thin top wall. In Fig. 6.1 a cross-section is shown of this reactor. The heaters are deposited on top of the thin channel top wall which consists of low stress silicon nitride (SiRN) or stoichiometric silicon nitride (Si₃N₄) on top of a heavily boron doped silicon (p⁺⁺Si) layer. The channel top wall consists of 0.15 μm SiRN and 0.85 μm p⁺⁺Si, or 0.20 μm
Si$_3$N$_4$ and 0.85 µm p$^{++}$Si for mechanical stability at elevated temperatures [3]. It was found that this reactor design has a limited operation window because of electrical breakdown of the SiRN and Si$_3$N$_4$ layers at elevated temperatures of 570 K and 870 K, respectively. At temperatures exceeding 570 K for the SiRN layer and 870 K for the Si$_3$N$_4$ layer, the thin layers lost their insulating properties and a short-circuit between the Pt-heaters and the conducting p$^{++}$Si layer was created. This short-circuit involves a large current flowing through the short-circuit path resulting in a very large temperature rise. Due to this temperature rise, the heater locally melts and the channel top wall is perforated. At these perforations, the rupture of the thin channel top wall is initiated by release of the intrinsic tensile stress and by the stresses caused by the large temperature gradient at the short-circuit. The p$^{++}$ Si layer should be omitted to prevent electrical breakdown of the SiRN or Si$_3$N$_4$ layers between the heaters and the conducting p$^{++}$ Si layer. However, microreactors with channel top walls consisting of 1 µm SiRN or Si$_3$N$_4$ only, show large thermally induced stresses at temperatures above 570 K [4, 5]. Due to these stresses, deformation of a flat channel top wall has been observed. This results eventually in failure of the top wall.

Arana et al. [6] built a suspended tube reactor which could be heated up to temperatures of 1203 K. The reactor contains two U-shaped channels which are connected to each other for heat exchange. These tubes are equipped with heater elements and are basically constructed of SiRN. The heated reaction channels are suspended at one side, and are allowed to expand and shrink freely, thereby reducing stress in the construction materials. Disadvantage of the reactor is the construction procedure, which is reported to be a very labor intensive process [7]. Another way of releasing the thermally induced stresses near the heater structures is by using a decoupling zone made of a corrugated layer [8, 9] as used in this study.

### 6.2 Reactor design

The reactor design is based on the previous microreactor design presented in chapter 3 for easy replacement in the experimental setup. The channel top wall of 1 µm, as shown in Fig. 6.1, is replaced by a more solid top wall of about
65 µm, in which a meandering SiRN tube is suspended, see Fig. 6.2. The heaters of the reactor are deposited inside these suspended tubes. In this figure cross-sectional drawings are shown of the suspended heater reactor. The connection wires of the heaters and the contact pads are sunk under the surface of the reactor chip. In Fig. 6.2 the suspended tubes of the temperature sensors are left out and only the heater tubes are shown for clearness.

In the previous microreactor prototypes, the heaters were deposited on top of a SiRN or Si₃N₄ dielectric layer on top of p⁺⁺ Si. In the new design, the heaters are deposited on a layer of SiRN only, and therefore no electrical breakdown can occur. The curved surface of the suspended tube provides a corrugated zone to decouple the thermal expansion of the heated bottom part of the tube from the rest of the reactor. The SiRN tubes, which contain the heaters, are the only elements of the reactor which are heated. Therefore, the catalyst is deposited only on the reaction channel side of these tubes.

In the production process [10] of these microreactors, first the pattern of the heaters, sensors and contact wires are etched into a silicon wafer. In this etched structure, 1 µm SiRN is deposited, which will form the suspended tubes. The SiRN trench structure, made in this way, is subsequently used as a built-in shadow mask to deposit the metal heater and sensor pattern on the bottom of the trenches. The SiRN tubes are then released by etching the flow channel on the reverse of the wafer. In this way, the depth of the flow channel will determine the final dimensions of the suspended tubes and therefore their strength. After catalyst deposition on the SiRN tubes, the flow channel is closed by bonding of a Pyrex baseplate with the gas inlet and outlet.

6.2.1 Thermal design

The suspended tubes not only prevent electrical breakdown and tube rupture by thermal stress, but they also thermally isolate the heaters. The suspended tubes are made of SiRN which has a low thermal conductivity of about 3 W m⁻¹K⁻¹ as compared to the value for silicon, 148 W m⁻¹K⁻¹ at 300 K. The solid heat conduction through the suspended tubes can be changed by changing the dimensions of the suspended tubes. The radius (r₁) of the curved sides of the SiRN tubes can be changed as well as the etching depth (dₑ), which determines
Figure 6.2: Cross-sections of the suspended heater reactor, not on scale. (a) The heaters are deposited on top of a meandering suspended SiRN tube. Underneath this meandering SiRN tube, the catalyst is positioned. (b and c) 3-dimensional cross-sections of the suspended heater reactor. The heater lines are sunk under the reactor chip surface on the SiRN tubes. Therefore, also the connection wires and the contact pads are sunk. In all pictures, the sensors are left out for clearness.
the part of the tube that is released, see Fig. 6.3. A heat balance was made over the cross-section of the tube to calculate the heater power needed to reach the reaction temperature of 1100 K. The catalyst that is deposited on the suspended tubes, will have a temperature, which is an average temperature over the catalyst width. The average catalyst temperature can be predicted when the lateral temperature profile of the suspended tubes is calculated. In the following, the temperature profile in the suspended tubes and the heat loss from them is calculated. Next to these, the thermal sensitivity to small changes in the released part of the SiRN tubes is investigated.

The SiRN tubes in which the heaters are deposited are suspended to a silicon layer of about 65 µm thickness, as shown in Fig. 6.3. It is assumed that at the edge where the tubes are suspended the temperature is equal to the temperature of the microreactor chip, due to the high thermal conductivity of silicon compared to that of SiRN. Solid heat conduction is taken only in one direction, over the width of the suspended tube wall because of the very large aspect ratio of the tubes. Heat losses from the top wall by conduction and/or convection to the gases inside and outside the reactor are taken into account as in chapter 3. Radiative heat losses are neglected. This assumption is validated with calculations presented at the end of this section. The 1-dimensional heat balance is made by stretching out the curved surface of the suspended tube as shown schematically in Fig. 6.3. The corresponding steady state heat balance is given by:

$$ l_t \delta \left( -\kappa \frac{dT_t}{dx} \bigg|_x + \kappa \frac{dT_t}{dx} \bigg|_{x+\Delta x} \right) + \frac{P}{w_t} \Delta x (1 - U(x - \frac{w_t}{2})) - $$

heat flow by convection to side walls  
heat flow by heater power  

$$ h_o(T_s - T_t)l_t \Delta x - h_i(T_i - T_t)l_i \Delta x = 0 $$

heat flow towards outside the reactor  
heat flow towards inside the reaction channel  
heat flow accumulation  

whereas the boundary conditions are:

$$ x = 0 \quad \frac{dT_t}{dx} = 0 $$

(6.2)

$$ x = \frac{u_t}{2} \quad T_t = T_s $$

(6.3)
Figure 6.3: Top drawing is a sketch of the channel top wall. At the bottom, a schematic representation is given of the stretched suspended tube as used in Eqs. 6.1 - 6.7.

in which $T_t$, $T_o$, and $T_i$ are the temperatures of the suspended tube, outside the reactor, and inside the reactor. $P$ is the heater power, $\delta$, $l_t$, and $w_t$ are the suspended tube thickness, length and stretched out width. $w_H$ is the heater width. $\kappa$ is the thermal conductivity of the suspended tube. The heat transfer coefficients $h_o$ and $h_i$ are for outside and inside the reactor, respectively. This heat balance is the same as for the flat top wall microreactors as solved in section 3.2.2.1 to give:

$$T_t = A \cosh(\sqrt{\beta} \hat{x}) - \frac{\alpha + \beta (T_g - T_s)}{\beta} \left( \cosh(\sqrt{\beta} \hat{x}) - 1 \right) + \frac{\alpha}{\beta} \left( \cosh(\sqrt{\beta} (\hat{x} - \epsilon)) - 1 \right) U(\hat{x} - \epsilon) + T_s$$  (6.4)

with:

$$A = \frac{\alpha \cosh \sqrt{\beta} - \cosh(\sqrt{\beta}(1 - \epsilon))}{\cosh \sqrt{\beta}} + (T_g - T_s) \frac{\cosh \sqrt{\beta} - 1}{\cosh \sqrt{\beta}}$$  (6.5)

$$\alpha = \frac{P w_t}{4 \delta \kappa \varepsilon l_t}$$  (6.6)
High temperature "suspended heater" microreactor

and

\[ \beta = \frac{h_{\text{tot}} w_t^2}{4 \delta \kappa} \]  

(6.7)

in which \( T_s \) is the temperature at the edge of the suspended tube, \( \hat{x} = \frac{2x}{w_t} \) a dimensionless coordinate, and \( \varepsilon = \frac{w_t}{w_t^*} \) the fraction heated of the tube wall. \( h_{\text{tot}} = h_o + h_i \) is the total heat transfer coefficient. \( T_g = \frac{h_o T_o + h_i T_i}{h_o + h_i} \) is the average gas temperature near the suspended tube.

In Fig. 6.4 the tube temperature \( (T_t) \) is plotted as a function of the dimensionless coordinate \( \lambda = \frac{\hat{x} + 1}{2} \), i.e. the origin defined at the left side wall, for different etching depths \( d_e \).

![Figure 6.4: Temperature in the suspended tube (T) as a function of the dimensionless width (λ) for different \( d_e \) with \( P = 1.5 \) W, and \( r_t = 5 \) µm.](image)

In Fig. 6.4 it can be seen that increasing \( d_e \), i.e. releasing more of the tubes, leads to an increase of the maximum temperature. The increase of the temperature is the result of the smaller solid heat conduction caused by the longer conduction pathway through the suspended heater tube. The reaction temperature needed for CPO of methane of 1100 K can be reached with \( d_e = 10 \) µm and a heating power \( P = 1.42 \) W. To check the above model calculations a 2-dimensional model of the channel top wall and suspended tube is made using the finite elements code FEMLAB [11], as shown in Fig. 6.5(a). In the 2-D FEMLAB model, heat loss by radiation from the reactor can be taken into account to calculate the influence of radiation on the reactor temperature. The dimensions of the suspended tube and channel top wall used in the calculation are the dimen-
Experimental

sions of the realized microreactor (see below), i.e. \( d_e = 6 \, \mu \text{m}, \ 2r_t = 10 \, \mu \text{m}, \) and \( w_H = 50 \, \mu \text{m}. \) In Fig. 6.5(b) the relative heat flow rates, calculated with the 2-D FEMLAB model, are given for solid heat conduction \( Q_{\text{con}}/P, \) forced convection \( Q_{\text{for}}/P, \) natural convection \( Q_{\text{nat}}/P, \) and radiation \( Q_{\text{rad}}/P \) as a function of the power dissipated in a heater \( P. \) From Fig. 6.5(b) it can be seen that more than

\[
\begin{align*}
Q_{\text{con}}/P & = 1.5, \\
Q_{\text{for}}/P & = 0.5, \\
Q_{\text{nat}}/P & = 0.1, \\
Q_{\text{rad}}/P & = 0.05
\end{align*}
\]

Figure 6.5: (a) Sketch of the realized suspended tube microreactor with: \( d_e = 6 \, \mu \text{m}, \ 2r_t = 10 \, \mu \text{m}, \) and \( w_H = 50 \, \mu \text{m}. \) (b) Relative heat flow rates for conduction \( Q_{\text{con}}/P, \) forced convection \( Q_{\text{for}}/P, \) radiation \( Q_{\text{rad}}/P, \) and natural convection \( Q_{\text{nat}}/P \) as function of dissipated heater power \( P \) calculated with the finite elements code FEMLAB [11].

80\% of the heat supplied by the heaters goes to the channel side walls by solid heat conduction. At a heating power of 1.5 W the calculated temperature at the heater is 1180 K, resulting in 3.5\% heat loss by radiation. The heat loss by radiation appears to be small as only a small part of the reactor is at a high temperature.

6.3 Experimental

The suspended heater reactor is based on the existing layout of previous reactor prototypes presented in chapter 3. The same microreactor housing is therefore
used as connections for the heaters, sensors, and gas in- and outlet are at the same positions. The reactor chip is kept at a constant temperature by the reactor housing in the same way as with previous microreactors to prevent water condensation during reaction. In Fig 6.5(a) a schematic representation of the suspended tube is given with the dimensions of the realized reactor: \( d_e = 6 \mu m \), \( 2r_t = 10 \mu m \), and \( w_H = 50 \mu m \). Experiments with the reactor have been performed to test the heaters electrical stability during heating. Heaters made of platinum, both with and without a tantalum adhesion layer are tested. The tantalum layer enhances the adhesion of the platinum film on the SiRN-tubes, but can also cause drift in electrical properties of the thin film [12]. The fabricated reactors were not suitable for catalytic reactions, because there was no catalyst inside the reaction channel yet. During the production process of the suspended tube microreactors, deposition of the Rh catalyst failed and no Rh was deposited inside the reaction channel. However, flammable mixtures of hydrogen and oxygen were fed to the reactor at elevated temperatures to test if these gas mixtures could be handled safely without gas phase reactions inside the small reaction channel.

### 6.4 Results and discussion

#### 6.4.1 Heater stability

The sensors and heaters have their own suspended tube and are thermally isolated form each other. The sensors therefore measure the temperature of the gas inside the reaction channel instead of the temperature of the heated tubes. Temperature readings with the heaters are possible, by using the resistance of the heaters as indication for the temperature. These resistance readings need to be corrected for the resistance of the connection wires. At MESA+ Research Institute similar heater structures were tested with a 4-point resistance measurement. In this way, the resistance of the connection wires is excluded from the measurements and the resistance of the connection wires can be determined. It was found that the resistance of the connection wires is 42% of the total resistance for the first and last heater of the reactor and 31% for the other three heater elements.
In Fig. 6.6 the results of a duration test are shown for heaters made of 200 nm Pt and of 200 nm Pt on top of 10 nm Ta. Both heaters were used at 1.7 W of heating power, resulting in a temperature above 800 K. Electrical stability of the thin film heater lines was obtained after pretreating the heaters at a higher heating power of 1.8 W than the operation heating power of 1.7 W. The Ta/Pt-heaters failed operation after 27 hours due to physical degradation. The thin metal film of the Ta/Pt-heaters agglomerated to small electrically isolated particles. The Pt-heaters were tested for 110 hours without failure at approximately 900 K. After the experiment, calibration of the Pt-heaters showed that the resistance and the thermal resistivity coefficient decreased with 2% and 0.7%, respectively. The small decrease of the resistance and the thermal resistivity coefficient proofs the long-term stable operation of the suspended tube reactor with Pt-heaters.

In the setup at TU/e laboratory, less heat can be supplied to the heaters (1.2 W maximal). The reactor housing was heated to 453 K and the heaters were set at 1.2 W for 1 hour, to gain stable temperature readings. Calibration of the heaters, by heating the reactor housing between 297 K and 453 K resulted in a temperature resistance coefficient of $0.00230 \pm 0.00006 \, \text{K}^{-1}$. In Fig. 6.7 the measured and calculated temperatures as a function of the heating power ($P$) are plotted. The calculated temperatures as a function of the heating power were obtained with both Eqs. 6.4 -6.7 and the FEMLAB model. In Fig. 6.7 it can be seen that
both models deviate significantly from the measurements. As mentioned before, most of the heat dissipated in the heaters is lost by conduction through the SiRN tubes. This makes the model sensitive to small errors in $\kappa$ and the thickness of the suspended tube wall. In the calculations a value of $\kappa = 3 \text{ W m}^{-1}\text{K}^{-1}$ is used. However, the thermal conductivity of SiRN strongly depends on the deposition process and reported values range from 1.2 to 13 W m$^{-1}$K$^{-1}$ [13]. In Fig. 6.7 the dotted line is calculated with a fitted $\kappa$ of 5.6 W m$^{-1}$K$^{-1}$ for the SiRN suspended tube which is within the range reported in literature. The deviation of $\kappa$ can be caused by oxidation of the SiRN tubes at high temperatures. Next to this, the thermal conductivity is taken as a constant in the calculations but is likely to be a function of temperature as the thermal conductivity of Si is.

The maximum supply power which can be dissipated with the heaters was determined by slowly increasing the power to the heaters. In Fig. 6.8 the resistance as a function of the supply power is shown. Heaters made of 200 nm Pt and 10 nm Ta / 200 nm Pt failed operation at 2.02 W and 2.74 W, respectively. The Pt-heaters were first used for the duration tests shown in Fig. 6.6 and therefore likely failed operation at a lower heating power compared to Ta/Pt-heaters. Temperature estimations with these heaters are difficult because the electrical
properties of the heaters depend on the heating history. Calibration after the experiments was not possible because both tests were destructive for the microreactors. An indication of the temperature, based on the color change of the glowing heaters, is given in Fig. 6.8. In the figure it can also be seen that the heater resistance changed gradually up to approximately 1000 K. After the color change from dark orange to glowing orange the heater resistance changed more than proportional with increasing heating power. The temperature can be expected to be approximately 1000 - 1100 K. Increasing the heating power resulted eventually in a white flash and heater failure. Heater failure at high temperatures is caused by physical degradation as the thin film agglomerates. It is expected that heaters made of Pt can be operated at 1100 K for several hours, which is sufficient for CPO of methane.

### 6.4.2 Hydrogen oxidation

The reactor is tested for safe handling of hydrogen oxygen mixtures at elevated temperatures. Feeding 42 ml/min of a flammable gas mixture of 24% H₂ and 12% O₂ in He to the microreactor, it was tested if gas phase reactions could be initiated. The reactor was tested by feeding the H₂ / O₂ / He mixture and
slowly increasing the heater power. At the maximum supply power of 1.2 W, i.e. at a top layer temperature of 785 K, no water was formed, indicating that no reactions occurred in the reaction channel. This indicates that in this type of microreactor highly explosive gas mixtures can be handled safely at high temperatures.

6.5 Conclusions

In this chapter, experiments with a high-temperature microreactor are presented. The microreactor is equipped with heaters deposited inside SiRN tubes which are suspended inside the flow channel. Previously used microreactors had a limited operation temperature up to 870 K. Reactor failure occurred at the heaters due to electrical breakdown of silicon nitride in the heated channel wall. To prevent the electrical breakdown, the heaters are suspended in SiRN tubes. The SiRN tubes form a corrugated wall which releases thermally induced stresses.

A reactor with suspended SiRN tubes containing Pt-heaters is operated stably for 110 hours at 900 K. At temperatures exceeding 1000 K, the heaters started to degrade, leading to shorter live times. It is expected that a suspended heater reactor with heaters made of platinum can be used up to 1100 K for several hours. This temperature would be sufficient to conduct catalytic partial oxidation of methane. Flammable mixtures of hydrogen and oxygen could be used safely inside the reactor. No hydrogen was oxidized up to a temperature of 785 K.

Nomenclature

- \( d_e \): etching depth to release tube \((\text{m})\)
- \( h \): heat transfer coefficient \((\text{W m}^{-2} \text{K}^{-1})\)
- \( l_s \): length of suspended tube \((\text{m})\)
- \( P \): power \((\text{W})\)
- \( Q_{\text{con}} \): heat flow rate by conduction \((\text{W})\)
- \( Q_{\text{for}} \): heat flow rate by forced convection \((\text{W})\)
- \( Q_{\text{nat}} \): heat flow rate by natural convection \((\text{W})\)
- \( Q_{\text{rad}} \): heat flow rate by radiation \((\text{W})\)
References

\[ r_t \] suspended tube radius \hspace{1cm} (m)
\[ R \] resistance \hspace{1cm} (Ohm)
\[ t \] time \hspace{1cm} (s)
\[ T \] temperature \hspace{1cm} (K)
\[ w_H \] width of heater \hspace{1cm} (m)
\[ w_t \] width of stretched tube \hspace{1cm} (m)
\[ x \] length scale, coordinate \hspace{1cm} (m)

Greek symbols
\[ \alpha \] defined by Eq. 6.6 \hspace{1cm} (K)
\[ \beta \] defined by Eq. 6.7 \hspace{1cm} (-)
\[ \delta \] thickness of the top wall \hspace{1cm} (m)
\[ \varepsilon \] heated fraction of the top wall \hspace{1cm} (-)
\[ \kappa \] thermal conductivity \hspace{1cm} (W m\(^{-1}\) K\(^{-1}\))
\[ \lambda \] dimensionless length scale \hspace{1cm} (-)

Subscripts
\[ g \] gas
\[ i \] inside the channel
\[ o \] outside the channel
\[ s \] side wall
\[ t \] top wall
\[ \text{tot} \] total

References


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In this chapter the main conclusions of this thesis are summarized and discussed. Aspects which can be used for further improvement and research on silicon based microreactors are addressed.
7.1 Conclusions / discussion

7.1.1 Thin film catalysts on silicon substrates

Thin film rhodium catalysts have been studied on flat silicon substrates. The rhodium catalysts were sputter deposited on different interlayers grown on top of silicon substrates viz. Ta/SiO$_2$, SiO$_2$/Si, Si$_3$N$_4$/Si, and SiRN/Si. Next to these sputtered catalysts, rhodium catalysts were prepared by wet chemical impregnation through spin coating of SiO$_2$/Si and quartz substrates. Rh catalysts on the different supports were used for hydrogen oxidation (473 K) and catalytic partial oxidation (CPO) of methane (1000 - 1200 K). For both reactions catalyst activity was measured in time. Although an initial high conversion is observed, after 1-2 hours on stream, no catalytic activity can be observed anymore, for most of the substrates, and for both reactions. CPO of methane to synthesis gas was found best on SiRN interlayers, giving high conversion and selectivity: $X_{O_2} = 97\%$, $X_{CH_4} = 57\%$, $S_{H_2} = 0.72$, and $S_{CO} = 0.80$. The chemical composition of the substrates outer surface was examined by TOF-SIMS experiments. It is revealed that silicon containing components from the substrates diffuse through the rhodium layer to the surface during both reactions. The silicon on the surface eventually blocks the entire surface, deactivating the catalyst.

7.1.2 Silicon based microreactors

The design of a silicon based microreactor with integrated heaters and temperature sensors for the catalytic partial oxidation of methane is presented. The microreactor design is based on a square channel closed at the top side by a thin silicon wall of approximately 1 µm. On top of this thin wall, heaters and temperature sensors are positioned. The catalyst is placed on the inside of the channel on the thin top wall. In this way a good thermal contact is realized to measure the catalyst temperature directly. This configuration enables a high temperature inside the reactor while stable connections for the gas inlet and outlet and electrical connections can be maintained at a lower temperature.

Catalytic partial oxidation of methane on a rhodium catalyst gives high conversion and selectivity at a temperature of 1100 K. Approximately 1.5 W of
heating power must be released by each of the 5 heaters, to reach the reaction
temperature in the middle of the channel top wall of 1100 K, while the rest of
the reactor is kept at 350 K. Calculations and experiments showed that fast heat-
ing and cooling of the reactor are possible with a time constant in the order of
0.5 ms. This fast response enables fast start-up, shut-down, and quenching of
the chemical processes inside the reactor.

Experiments have been performed with different microreactor prototypes to
test their design and the design models. A microreactor equipped with a chan-
nel top wall consisting of 200 nm Si$_3$N$_4$ and 850 nm p$^{++}$Si could be heated to a
temperature of 870 K. The temperature was limited by electrical breakdown of
the top wall resulting in failure of the reactor. With this reactor configuration,
hydrogen oxidation was performed at temperatures between 560-670 K because
the reaction temperature would be too low for CPO of methane. Flammable
mixtures of hydrogen and oxygen were safely oxidized with 100% conversion,
proving the safe operation of the microreactor. It was found that at these high
temperatures, the heaters and sensors electrical properties start to deviate due
to degradation. The high temperature degradation of the heaters and sensors
can be prevented by using the heaters and sensors at a higher temperature than
the operation temperature during the experiment.

The heat transport inside the microreactor is studied by means of model sim-
ulation and experiments. Nusselt and Sherwood correlations are derived as
function of the Graetz number. It was found that the heat transport is develop-
ing along a considerable length of the reaction channel. When the inlet gases
are colder than the channel side walls, the heat flux on the side walls reverses
and heat transport does not develop within the length of the channel. When
the inlet gases are at the same temperature as the side walls of the channel,
the asymptotic value of the Nusselt number is the highest and the develop-
ing length the shortest. A high Nusselt number results in a high heat transfer
coefficient which is preferred for kinetic research, as hot-spots and runaway re-
actions can be prevented. The mass transport limited CPO of methane is mod-
eled inside the square microreactor channel. A model is made, which can be
used for reaction kinetic research of this reaction. As no CPO experiments have
been conducted inside the microreactors, only modeling results are presented.
It was found that making use of helium instead of nitrogen as an inert gas in
the reactor feed results in a lower Reynolds number and therefore a lower local Sherwood number. Despite the lower Sherwood number, the mass transport is enhanced because the diffusion of the components is higher in helium than in nitrogen and therefore the conversion increases. In the reactor model, the Sherwood number is a function of the axial position inside the reactor. If the asymptotic Sherwood number of 2.43 would be used in the calculations, the calculated local conversion will be erroneous with deviations up to 4% in the conversion. The reaction channel is heated from the top side only and therefore a strong temperature gradient of $1.5 \cdot 10^6$ K/m exists. It is found that despite this strong temperature gradient, the influence of thermal diffusion on the conversion is negligible, simplifying the calculations.

In the flat top wall configuration, electrical breakdown of the silicon nitride layer occurs at elevated temperatures. Leaving out the electrical conducting $p^{++}$Si layer would solve this problem but would also make the top wall more vulnerable to mechanical breakdown due to thermal stresses. In a new reactor configuration, the heaters were suspended in SiRN tubes. The SiRN tubes serve as a corrugated zone, releasing mechanical stresses. These microreactors were operated for 110 hours at 900 K. It is expected that microreactors with heaters in SiRN suspended tubes can be operated at 1100 K for several hours.

7.2 Outlook

7.2.1 Catalytic layers on silicon support material

The tested catalyst platelets showed deactivation, except the catalyst inside the silicon microreactors. It is still not completely clear why the catalyst inside the microreactors did not deactivate, while deactivation does occur on silicon substrates. Inside the microreactors, the catalyst is deposited on a 1 µm thin layer consisting of 200 nm Si₃N₄ and 850 nm $p^{++}$Si. Next to this, the top wall with the catalyst will experience thermal stress during operation which might influence the deactivation process. It would be interesting to mimic the microreactor environment by making a flat platelet catalyst support with about the same electrical and mechanical properties. Using the suspended heater reactors, the catalysts is deposited on the SiRN tubes only. The catalytic activity of a com-
Combination of this support and deposited rhodium can be tested by making use of a SiRN wafer only i.e. not a silicon wafer with a SiRN layer on top of it. In this way, the rhodium catalyst can be studied for stability and surface chances during reaction conditions.

In literature, silicon based microreactors are often fixed-bed microreactors. These reactors contain catalytic particles with much more surface area and less contact to the silicon channel walls. Packed-bed reactors, however, have the disadvantage of less heat transport from the catalyst to the reactor walls. Heat build up, and therefore hot spot formation are likely to occur inside the bed. Because the catalyst has less contact with the silicon of the reactor walls, it can be argued that silicon diffusion from these walls is unlikely to occur. More catalyst surface area and slight contact with silicon can also be created by making use of Al$_2$O$_3$ wash coatings [1, 2], impregnation of an anodic oxidized Al$_2$O$_3$ layer [3], impregnation of oxidized porous silicon [4, 5], or zeolites [6–8] inside the silicon-based micro channel and on the catalyst support platelets. These porous layers still have some contact with the silicon support providing heat transport. Next to this, the porous structure can be expected to be more stable against the diffusion of silicon at elevated temperatures.

### 7.2.1.1 Material properties

To model the temperature profile inside the build silicon microreactors, the thermal conductivity of silicon, and silicon nitride needs to be known accurately. In the microreactor with the flat channel top wall 70-90%, and in the suspended heater reactor 85-95% of the heat provided by the heaters flows to the side walls of the channel. This makes the reactor models sensitive to errors in the thermal conductivity of the construction material, see sections 3.2.2 and 6.4.1. At elevated temperatures, parts of the reactor can be expected to oxidize. This oxidation process will change the physical properties of the materials used. For more accurate modeling of the catalyst temperature, the thermal conductivities of the construction materials need to be determined at the reaction temperature and after operation of the reactor at high temperatures.
7.2.1.2 Microreactor improvements

In the presented suspended heater microreactor concept, one line of heaters was used. By making use of two parallel heater lines, an isothermal zone can be created, in between these heaters. In this way each heater can be operated at a lower potential and current because each heater would only need to supply about half of the heating power. The lower power dissipation in each heater might enhance the heaters’ life time further. In Fig. 7.1 a sketch of such a reactor is given. The thermal stress is released and the area between the heater tubes is thermally insulated by using two corrugated zones. In Fig. 7.2(a) the
dimensions of the heater tubes are taken the same as for the reactor presented in chapter 6 and the distance between the corrugated tubes is taken 100 µm. Comparing the result with the results of the realized single heater microreactors it can be seen that about half of the energy is needed in one heater when two parallel heaters are used. The relative heat flow rates for conduction \( Q_{\text{con}} / P \), forced convection \( Q_{\text{for}} / P \),
Figure 7.2: (a) Average temperature ($T$) as a function of the total power supplied to the heater(s) ($P$). The solid line represents the average temperature calculated for the suspended heater reactor with two parallel heaters. The average temperature is calculated for the part of the top wall between the heaters. The dashed line is the average heater temperature for the suspended heater reactor as presented in Chapter 6. (b) Relative heat flow rates for conduction ($Q_{\text{con}}/P$), forced convection ($Q_{\text{for}}/P$), radiation ($Q_{\text{rad}}/P$), and natural convection ($Q_{\text{nat}}/P$) as a function of the dissipated heater power ($P$) for the suspended heater reactor with two parallel heaters.

Radiation ($Q_{\text{rad}}/P$), and natural convection ($Q_{\text{nat}}/P$) as a function of dissipated heater power ($P$) are plotted in Fig. 7.2(b). When this figure is compared to Fig. 6.5(b), the results of the realized microreactor, it is obvious that the heat flow rate by conduction has decreased while the heat flow rate by radiation has increased as a larger area is heated. The isothermal zone can be completely used for catalyst deposition, increasing the catalyst surface. The area between the corrugated zones can be extended by increasing the distance between them and by making use of extra parallel corrugated heater tubes.
References


List of publications

Journal publications


Conference proceedings


**Professional publications**

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Poul van Male was born on November 16th, 1974 in Knokke-Heist, Belgium. He finished Higher General Secondary Education at the comprehensive school ’t Zwin in Oostburg in 1993. In 1997 he obtained his B.Sc. in Chemical Engineering at the Faculty of Technology of West-Brabant Polytechnic, after which he continued his education at Eindhoven University of Technology. He obtained his M.Sc. in Chemical Engineering on the topic of "Dehydration performance of an amorphous silica pervaporation membrane" in 2000. In March 2000, he started working towards his Ph.D. degree at the Department of Chemical Engineering and Chemistry of Eindhoven University of Technology, in the Laboratory of Chemical Reactor Engineering. His work focused on the design, modeling, and testing of silicon technology-based microreactors for high temperature gas phase reactions. Currently, he is working as a process engineer at Royal Haskoning Dordtse Engineering in Dordrecht.