DESIGN OF A MICROREACTOR FOR REACTIONS USING SUPERCRITICAL FLUIDS AS THE REACTION SOLVENT

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presented by
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So kam es, dass ich mich bei ihm und bei vielen der Anwesenden verhasst machte; bei mir selbst aber dachte ich, als ich weggging: "Im Vergleich zu diesen Menschen bin ich der Weisere. Denn wahrscheinlich weiss ja keiner von uns beiden etwas Ordentliches und Rechtes; er aber bildet sich ein, etwas zu wissen, obwohl er nichts weiss, während ich, der ich nichts weiss, mir auch nichts zu wissen einbilde. Offenbar bin ich im Vergleich zu diesem Mann um eine Kleinigkeit weiser, eben darum, dass ich, was ich nicht weiss, auch nicht zu wissen glaube." Dann ging ich zu einem anderen, zu einem, der noch weiser galt als mein erster Mann.

Platon, Apologie des Sokrates, Erste Rede, 21d
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Abstract

The high surface-to-volume ratio of microreactors offers an increased heat and mass transfer and the possibility to conduct high pressure reactions without the need of excessive reactor wall thickness for a safe operation. This thesis presents an experimental study of the fabrication and characterization of a silicon/glass microreactor suitable for reaction conditions using supercritical $CO_2$ ($scCO_2$) as reaction solvent. The performance of a packed bed microreactor was analyzed for the case of the continuous heterogeneously catalyzed hydrogenation of cyclohexene. Reaction rates were compared with conventional reactors for the case of a gas-liquid-solid and a supercritical fluid (SCF)-solid reaction. The thesis further describes the fabrication and the mechanical stability of the microreactor and its microfluidic connections at high pressure and temperature. The optical access into the microreactor at high pressure enables the in situ characterization of flow pattern, phase behavior and chemical composition.

The high thermal conductivity of Si, the good micromachinability, high mechanical strength and the optical transparency of glass led to the decision to fabricate a Si/glass microreactor using photolithography, dry etching and anodic bonding techniques. The microfluidic connections, highly stressed due to mechanical, thermal and handling loads, were fabricated using metallic solder to attach capillaries onto the Si/glass chip.

A detailed mechanical characterization of the microfluidic connections by tensile, pressure and leak tests showed the feasibility of such connections for combined high pressures and temperatures of 140 bar and 80
in continuous operation. An analytical mechanical examination of the rectangular microfluidic channels defined a largest possible channel width for high pressure applications at 150 bar in the Si/glass microreactor of 400 µm.

Using laser induced fluorescence and confocal laser scanning microscopy a fluid dynamic characterization of the packed bed microreactor was performed. Residence time distribution measurements showed the influence of particles and gas content on dispersion in the microchannel. A determination of the liquid film thickness in a two phase gas-liquid flow evaluated the part of liquid passing the packed bed in the near wall region of high porosity.

Mass transfer and the reaction performance were studied in the case of the solid catalyzed hydrogenation of cyclohexene. The high pressure reaction at gas-liquid-solid flow conditions showed a mass transfer limitation. The liquid slug velocity at different pressures was measured. The mass transfer resistance was decreased by using supercritical CO₂ as reaction solvent. In situ phase studies ensured a single phase behavior of the reaction mixture and confirmed the complete solubility of the reactants in CO₂.

To take advantage of the favorable possibilities in terms of precise control of temperature, pressure and mixing in situ Raman spectroscopy measurements were conducted in the presented continuous microreactor system. These results showed the wide range of applications in the field of in situ online chemical reaction analysis at high pressure and temperature on chip.
Zusammenfassung


Zusammenfassung


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**Nomenclature**

### Abbreviations

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<thead>
<tr>
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<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASE</td>
<td>Advanced Silicon Etch</td>
</tr>
<tr>
<td>AU</td>
<td>Airy Unit</td>
</tr>
<tr>
<td>BET</td>
<td>Brunner, Emmet, Teller</td>
</tr>
<tr>
<td>CTE</td>
<td>Coefficient of Thermal Expansion [$K^{-1}$]</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>DI</td>
<td>Deionized</td>
</tr>
<tr>
<td>DRIE</td>
<td>Deep Reactive Ion Etching</td>
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<tr>
<td>FOV</td>
<td>Field of View</td>
</tr>
<tr>
<td>fps</td>
<td>Frames per Second</td>
</tr>
<tr>
<td>HMDS</td>
<td>Hexamethyldisilazan</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductive Coupled Plasma</td>
</tr>
<tr>
<td>i.d.</td>
<td>inner diameter</td>
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<tr>
<td>LIF</td>
<td>Laser Induced Fluorescence</td>
</tr>
<tr>
<td>LSM</td>
<td>Laser Scanning Microscopy</td>
</tr>
<tr>
<td>MEMS</td>
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</tr>
<tr>
<td>MST</td>
<td>Microsystem Technology</td>
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<td>PDMS</td>
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Nomenclature

PMMA  Polymethylmethacrylate
PVD   Physical Vapor Deposition
RT    Room Temperature
RTD   Residence Time Distribution
SCF   Supercritical Fluid
SCWO  Supercritical Water Oxidation
SEM   Scanning Electron Microscope
µTAS  Micro Total Analysis Systems

Greek Letters

\( \alpha \) \( [Wm^{-2}K^{-1}] \) heat transfer coefficient
\( \alpha \) \([-\]\) aspect ratio
\( \gamma \) \( [Jm^{-2}] \) specific surface energy
\( \delta \) \([m]\) liquid film thickness
\( \epsilon \) \([-\]\) void fraction
\( \epsilon \) \([-\]\) dielectric constant
\( \varepsilon \) \([J]\) molecular energy
\( \eta \) \([Pas]\) dynamic viscosity
\( \lambda \) \([Wm^{-1}K^{-1}]\) thermal conductivity
\( \nu \) \([m^2s^{-1}]\) kinematic viscosity
\( \nu \) \([-\]\) Poisson ratio
\( \rho \) \([kgm^{-3}]\) density
\( \theta \) \([-\]\) dimensionless time
\( \sigma \) \([MPa]\) mechanical flexural stress
\( \sigma \) \([Nm^{-1}]\) surface tension
\( \tau \) \([MPa]\) mechanical shear stress
\( \tau \) \([s]\) characteristic time

Latin Letters

\( A \) \([m^2]\) area
\( a \) \([-\]\) Ergun coefficient
<table>
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<th>Symbol</th>
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<td>conversion</td>
</tr>
<tr>
<td>x</td>
<td></td>
<td>coordinate</td>
</tr>
<tr>
<td>y</td>
<td></td>
<td>coordinate</td>
</tr>
<tr>
<td>z</td>
<td></td>
<td>coordinate</td>
</tr>
</tbody>
</table>
Sub- and superscripts

A  activation
a  area
amb ambient
app apparent
b  bending
c  capillary, characteristic, critical
cat catalyst
E  effluent
eff effective
em emitting
exc exciting
f  flexural
G  gas
h  hydraulic
L  length, liquid
l  liquid
m  mass
max maximum
min minimum
o  outer
obs observed
out outlet
p  particle
pb packed bed
i  inner
in inlet
R  reactor
s  solid
tot total
v  volumetric
w  wall
Chapter 1

Introduction

1.1 Motivation and thesis overview

The combination of small reactor scales and high pressure offers new insights into chemical reaction technology and is the driving force of this thesis. The reduction of the characteristic length scales — and with this the increase of the surface-to-volume ratio — is advantageous for several important mechanisms in chemical reaction engineering. Among these are the mechanical stability and increased heat and mass transfer. In high pressure chemical reaction engineering supercritical fluids have attracted enormous interest as solvents for chemical reactions. Fluids above their critical temperature and pressure show no phase boundaries and an increased solubility. This thesis combines the unique synergies of microreactors and supercritical fluids (SCFs), which lead to novel process concepts. For the case of a solid catalyzed model reaction the advantages of such a system compared to macroscale reactors is shown.

The thesis is organized as follows. Each chapter can be read independently and shows a closed view on the specific part of the whole thesis. This chapter introduces the reader into the thesis subject of microreactors and supercritical fluids. A literature review is included in the
section “State of the art”. The presentation of the objectives of the thesis concludes the introduction.

Chapter 2 ”Fabrication” gives an overview of different materials which can be microfabricated and used for microreactor fabrication. Further it explains our choice for silicon and glass as reactor materials. The fabrication process of the Si/glass microreactor and the microfluidic connections is described in detail. Different catalyst incorporation methods are shown.

Chapter 3 ”Mechanical Characterization” includes the experimental and analytical mechanical analysis of pressurized microchannels and the microfluidic connections. Pressure and tensile tests at elevated temperature indicate the mechanical strength of the microfabricated device.

Chapter 4 ”Fluid Dynamic” describes the theoretical background of fluid flow in small dimensions. Optical measurements such as Laser Induced Fluorescence (LIF) and confocal Laser Scanning Microscopy (LSM) used for characterizing the fluid flow in rectangular microfluidic channels are explained. Liquid film thickness and residence time distribution in multiphase flow are addressed.

Chapters 5 ”High Pressure Reactions” is dedicated to the experiments of the solid catalyzed hydrogenation at high pressure. An overview of reaction analysis for heterogeneous catalysis in terms of mass transfer is given. The performance of the chemical reaction in case of a three phase and of a two phase reaction with supercritical $CO_2$ is analyzed and compared with macroscale counterparts.

Chapter 6 ”Summary and Outlook” concludes the thesis and provides an outlook into future work. First experiments with in situ Raman spectroscopy show the potential in the field of continuous chemical reaction analysis with high pressure microreactors.
1.1 Motivation and thesis overview

1.1.1 Microreactors

Microfabricated chemical systems are of increasing interest in a variety of chemical, pharmaceutical and biological applications such as: micro heat-exchangers, miniaturized chemical analysis systems and microreactors. The traditional chemical industry uses larger equipment scales to achieve cost-efficient production (economy of scale). Parallel processing with microfabricated chemical systems has the potential to provide cost benefits. Moreover it has other advantages such as better control of temperature and reaction outcome — yield and selectivity for products — that are often difficult to achieve in large scale systems.

Microreactors have several advantages compared to macroscale applications (Lerou et al., 1995; Ehrfeld et al., 2000; Jensen, 2001). A high surface-to-volume ratio — 4-5 orders of magnitude greater than a conventional batch reactor — enhances heat and mass transfer. Since the diffusion time scale is proportional to the square of the characteristic length, diffusion mixing is better facilitated depending on the characteristic length scale of microreactors. Mixing in microfluidic systems is further enhanced in multiphase flow, static mixers or patterned flow channels. The high heat transfer rates that are possible because of the large surface-to-volume ratio reduce thermal gradients in microchannels. This advantage is especially useful to control the adiabatic temperature rise during exothermic chemical reactions. The partial or total elimination of hot spots enhances process safety by ameliorating thermal runaway. Additionally, the hold-up of potentially hazardous reactants is minimal. The ability to produce on demand eliminates the need for storage of aggressive and toxic intermediates or explosives in large volumes. These advantages are attractive from an economic as well as from a safety point of view. Silicon and glass microreactors provide optical access into the reaction channel and therefore an insight to the phase behavior of reactions using SCFs as reaction solvent. Hence, it is possible to analyze the flow, the phases and reaction species under reactive conditions in a defined volume.

The following two examples demonstrate the influence of decreasing length scale on the phenomena of mechanical strength and mass transfer.
The mechanical stress in the walls of a reactor vessel under inner pressure\(^1\) can be easily derived from the momentum balance in a pressurized cylinder. Equation 1.1 describes the circumferential stress \(\sigma_\varphi\) in the wall of the reactor vessel

\[
\sigma_\varphi = \frac{p_i d_i}{2s}
\]

with \(p_i\) the pressure inside the cylinder, \(d_i\) the inner diameter and \(s\) the wall thickness. The stress in the wall is therefore reduced by decreasing the inner diameter of the cylinder and a smaller wall thickness is necessary to withstand a certain pressure.

Due to the small characteristic length scales, mixing processes in microreactors often take place in laminar flow. Hence, molecular diffusion is the dominant transport phenomenon in these systems. The characteristic diffusion length \(x\) by molecular diffusion is described as

\[
x = \sqrt{c D_\infty \tau}
\]

where \(D_\infty\) is the molecular diffusion coefficient, \(c\) a geometry factor and \(\tau\) the characteristic diffusion time. Consequently, a reduction in size leads to a faster diffusion and therefore a mass transfer within a short time.

### 1.1.2 Supercritical fluids in reaction engineering

Supercritical reaction systems are gaining acceptance in the chemical industry. DuPont has announced a 40 million US$ demonstration plant for supercritical polymerization. A large-scale (1000 \(ty^{-1}\)) supercritical hydrogenation plant was commissioned by Thomas Swan and Company in the U.K. in 2002. During the last decade, supercritical fluids — such as supercritical carbon dioxide and supercritical water (\(scH_2O\)) — have

\(^1\)with the simplification of thin walls and no boundary effects
been increasingly used as reaction media in order to conduct a variety of catalytic reactions, such as hydrogenations, alkylations, aminations and oxidations (Grunwaldt et al., 2003; Jessop, 1999). While a number of supercritical co-solvents have been investigated — a compiled list of 26 different supercritical fluids and their properties can be found in (Jessop, 1999) — only a few of them show ”mild”critical parameters, reasonable cost and could be considered as ”green”solvents. Carbon dioxide is often employed as the preferred choice because it has mild critical properties ($T_c = 30.9 \, ^\circ C$, $p_c = 73.8 \, bar$), is non-toxic, non-flammable and inexpensive. The physical and transport properties of supercritical fluids can be drastically altered from gas-like to liquid-like behavior by simply isothermally varying the pressure in the region near the critical pressure ($p_c$). Such pressure-tuning yields to fluids with unique properties that have been exploited in catalysis in a variety of ways such as:

- enhanced desorption and transport of heavy molecules — such as coke precursors — in mesoporous catalysts alleviating pore-diffusion limitations and improving catalyst effectiveness

- \textit{in situ} removal of primary products, stabilizing primary product selectivity

- elimination of oxygen or hydrogen solubility limitations in the liquid phase, thereby eliminating interphase mass transfer resistances in multiphase reaction systems

- enhanced heat capacity improving the problem of parametric sensitivity in exothermic fixed-bed reactors.

Moreover, there are a number of factors that make the use of supercritical carbon dioxide in reactors inherently safe. These factors are including the replacement of volatile organic solvents with non-flammable CO$_2$, pressure-tunable heat capacity that avoid reactor runaway and increased reaction rates that minimize hold-up. Operating a reactor at supercritical conditions may therefore be viewed as an excellent example of the multifunctional reactor concept.
Additionally, the fluid characteristics of SCF are beneficial for chemical reactions such as increased solubility, high diffusivities and the ease of product separation after the reaction (Baiker, 1999). Several of these advantages have been demonstrated for various types of heterogeneously catalyzed reactions spanning a wide spectrum of chemical industries including petrochemicals, fine chemicals, food, agricultural chemicals and pharmaceuticals.

1.2 State of the art

The miniaturization of chemical devices has been studied for many years. Among the first (Manz et al., 1990; Ramsey et al., 1995; Brody et al., 1996; van den Berg and Lammerink, 1998) explored the possibility of biotechnology in microscale continuous flow systems. This was mainly done for analytical tests because the temperature could be rapidly cycled and the sample volume was extremely small. The goal of an integrated laboratory in a microfluidic device — the micro Total Analysis System (μTAS) — was the driving force for exploring microscale chemical devices. As knowledge of fluid dynamics and multiphase flow characteristics in microchannel systems increased, chemical reactions in microsystems have become interesting for chemical and pharmaceutical applications. Both single- and multiphase reactions in microfluidic systems have been reported in literature (Jensen, 2001; Hessel et al., 2003; Wada et al., 2006). In particular, the direct fluorination (de Mas et al., 2003; Jähnisch et al., 2000) and reactions conducted in the explosive regime where the small channels suppress the homogeneous gas phase reaction which would lead to a kinetic explosion (Veser, 2001; Inoue et al., 2007), showed the potential of microreactors with superior temperature control and improved the safety of hazardous reactions.

Different materials and fabrication techniques have been reported for the design of microfluidic devices. Microreactors made of silicon and glass use microfabrication methods including multiple photolithographic and etch steps and anodic bonding (Jensen, 2006). The fabrication

\(^2\)higher than in liquids
steps are known from the microelectromechanical systems (MEMS) technology (in Europe also called: microsystems technology (MST)) and are widely used for microfluidic and microreaction devices (Verpoorte and De Rooij, 2003). Silicon based microstructures including micro machinery (micro engine, micro turbine) that withstand high pressure and high temperature have been known for several years (Epstein and Senturia, 1997). MEMS technology requires cleanroom facilities and aggressive chemical substances are involved to manufacture microstructured devices. This has a negative impact on the life cycle analysis of MEMS-based microreactors (Wälchli, 2005) and has to be considered compared to other fabrication methods.

In many biological applications, a variety of polymers can be used as material for microfluidic channels; e.g. epoxy, polyethylene (PE), polymethylmethacrylate (PMMA) and polydimethylsiloxane (PDMS) using soft-lithography (Xia and Whitesides, 1998). Metallic microreactors are fabricated with micromachining-, laser- or molding techniques. The so called LIGA process enables the fabrication of microstructures of metals, metal alloys, polymers and ceramics (Ehrfeld, 2002). Present investigations of reactions in microreactors deal with the parallel-screening capabilities of microreactors (Potyrailo and Amis, 2003) and the integration of sensors i.e. (Floyd et al., 2005).

Many examples of industrial microreactor production setups were presented recently, especially in the pharmaceutical and fine chemical sectors. Clariant produces up to 80 t of pigments per year using microreactor technology developed by Cellular Process Chemistry Systems GmbH (CPC). In 2004 the German project MicroChemTec presented a modular backbone system to integrate different microchemical devices in one set up. Microinnova designed a microreactor for a throughput of 3 $th^{-1}$ for the operation in production scale that started operating in 2005. DSM Fine Chemicals in collaboration with the Forschungszentrum Karlsruhe presented a 1.7 $th^{-1}$ throughput microreactor system in 2006. This microreactor system is fully integrated in the commercial chemical production. Plate based modular laboratory scale systems are commercially available from Ehrfeld Mikrotechnik BTS and the Fraunhofer Institut. In chemical applications metallic capillaries are used as tubular reactors. Fabrication methods for the combination of
high pressure and high temperature optically accessible microreactor devices are rare because of challenging mechanical requirements for the system.

The use of high pressure microreactors compared to macroscale counterparts is advantageous. No excessive wall thickness of the reaction channel is needed for mechanical stability and the impact of hazardous failure is drastically reduced since only small amounts of material are involved. Only few studies have discussed high pressure chemical reactions in continuous flow microreactors so far. Devices like precision high pressure pumps and back pressure regulators lead to high investment costs. Moreover high pressure microfluidic connections are not yet standardized for chip based microreactors and are still difficult to manufacture if different materials are involved. Most high pressure reactions in continuous flow microreactors are conducted in capillaries. This has several advantages such as standard high pressure fluidic connections, inexpensive tubing and an adjustable reactor volume depending on the length of the capillary. The main drawback is the lack of optical transparency in metallic tubes and that the integration of different operations such as mixing, heating and analysis cannot be carried out within one single device.

A quartz capillary reactor was designed and used for oxidation studies in supercritical water by (Maharrey and Miller, 2001b). The same authors performed online mass spectroscopy at the reactors outlet, designed as a nozzle (Maharrey and Miller, 2001a). A supercritical water microreaction setup made from Hastelloy capillaries is presented by (Ikushima et al., 2002). A silica fiber as microreactor is presented by (Benito-Lopez et al., 2005), where optical fibers are integrated via a cross-section for UV/Vis monitoring of the reaction. A "step-by-step-rapid-mixing and heating"microfluidic system of Hastelloy capillaries for reactions in high pressure and high temperature water was designed by (Kawanami et al., 2007). In conclusion the capillary based microreactor studies point out the inexpensive capillaries, the rapid heating and quenching, the ease of handling high pressures and the low energy consumption compared to macroscale high pressure setups.

Chip based planar microfluidic devices follow the concept of the full
integration of different units in one single chip. Precise micromachining possibilities enable the fabrication of \( \mu m \)-range features that are necessary for the design of passive mixing elements and flow control such as bubble formation. The most important advantage of glass or Si/glass as reactor material is the optical transparency. The more expensive fabrication compared to capillary reactors and the non standardized microfluidic connections may be accounted as drawbacks. Planar chip-type high pressure microreactors are rarely reported in literature. (Szekely and Freitag, 2004) presented a glass microreactor with O-ring press fittings. (Kobayashi et al., 2005) fed a premixed reaction mixture into a glass chip for the hydrogenation with sc\( CO_2 \) as the reaction solvent. Glass microreactor chips were also used by (Tiggelaar et al., 2007) performing high pressure reactions with liquid \( CO_2 \). Recently our laboratory performed a three phase hydrogenation in a Si/glass packed bed microreactor at high pressure (Trachsel et al., 2008). Table 1.1 summarizes high pressure reactions in continuous flow microreactors.
Table 1.1: Published high pressure reactions in continuous flow capillary based (1) and chip based (2) microreactors.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Experiment</th>
<th>Dimensions</th>
<th>Reactor material</th>
<th>Connection</th>
<th>Range</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>i.d. = 750 µm</td>
<td>Quartz</td>
<td>HPLC fittings</td>
<td>p = 280 bar</td>
<td>low energy required to reach sc conditions, online mass spectrometry</td>
</tr>
<tr>
<td></td>
<td>Oxidation of acetic acid in scH₂O</td>
<td>Vₚ = 148 µL</td>
<td></td>
<td></td>
<td>T = 530 °C</td>
<td></td>
</tr>
<tr>
<td>Maharrey and Miller (2001b, a)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acid catalyzed reactions in scH₂O</td>
<td>i.d. = 250 µm</td>
<td>Hastelloy C-276</td>
<td></td>
<td>p = 400 bar</td>
<td>possible production of 0.25 kg/d ε-caprolactam</td>
</tr>
<tr>
<td>Ikushima et al. (2002)</td>
<td></td>
<td>Vₚ = 50 µL</td>
<td></td>
<td></td>
<td>T = 400 °C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Online UV/Vis spectroscopy in capillary</td>
<td>Vₚ = 3 µL</td>
<td>Silica</td>
<td>HPLC fittings</td>
<td>p = 600 bar</td>
<td>used conventional HPLC tools</td>
</tr>
<tr>
<td>Benito-Lopez et al. (2005)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(continued)
Table 1.1: Continued.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Experiment</th>
<th>Dimensions</th>
<th>Reactor material Connection</th>
<th>Range</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kawanami et al. (2007)</td>
<td>C-C coupling reactions in water</td>
<td>$i.d. = 500 \mu m$</td>
<td>Hastelloy C-276</td>
<td>$p = 250 \text{ bar}$</td>
<td>step-by-step rapid mixing and heating microreaction system</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$V_R = 3.5 - 1178 \mu L$</td>
<td></td>
<td>$T = 250 \degree C$</td>
<td></td>
</tr>
<tr>
<td>(2) Chip based microreactors</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Szekely and Freitag (2004)</td>
<td>Monolithic stationary phase in microchannel</td>
<td>$w = 80 \mu m$</td>
<td>Glass</td>
<td>$p = 150 \text{ bar}$</td>
<td>no cleanroom facilities needed</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$h = 70 \mu m$</td>
<td>O-ring press fittings</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kobayashi et al. (2005)</td>
<td>Hydrogenation with $scCO_2$</td>
<td>$d_h = 133 \mu m$</td>
<td>Glass</td>
<td>$p = 90 \text{ bar}$</td>
<td>high reaction productivity within 1 s</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$V_R = 8 \mu L$</td>
<td></td>
<td>$T \approx 60 \degree C$</td>
<td></td>
</tr>
<tr>
<td>Tiggelaar et al. (2007)</td>
<td>Carbamic acid formation with liquid $CO_2$</td>
<td>$d_h = 42 \mu m$</td>
<td>Borosilicate glass</td>
<td>$p = 400 \text{ bar}$</td>
<td>in-plane microfluidic connections</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$V_R = 0.3 \mu L$</td>
<td>Epoxy glued silica fibers</td>
<td>$T = 100 \degree C$</td>
<td></td>
</tr>
</tbody>
</table>

(continued)
<table>
<thead>
<tr>
<th>Reference</th>
<th>Experiment</th>
<th>Dimensions</th>
<th>Reactor material Connection</th>
<th>Range</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benito-Lopez et al. (2007)</td>
<td>Esterification with (\text{scCO}_2) as Tiggelaar et al. (2007)</td>
<td>(p = 110 \text{ bar})</td>
<td>(T = 100 \degree \text{C})</td>
<td>Significant rate enhancement using (\text{scCO}_2)</td>
<td></td>
</tr>
<tr>
<td>Trachsel et al. (2008)</td>
<td>Hydrogenation of cyclohexene, LIF</td>
<td>(d_h = 368 \mu m) (V_R = 3.4 \mu L)</td>
<td>Si/glass Soldered stainless steel tubing</td>
<td>(p = 140 \text{ bar}) (T = 80 \degree \text{C})</td>
<td>Packed bed microreactor, mass transfer limited</td>
</tr>
</tbody>
</table>
1.3 Thesis objectives

The combination of the enhanced heat and mass transfer properties and the mechanical stability of microreactors with the unique fluid properties of supercritical reaction media, including elimination of gas/liquid phase boundaries, provide unique and unparalleled synergies for novel exploitation in microreaction engineering. The challenge of developing a new environmentally beneficial and inherently safe catalytic reaction system by combining the properties of microscale structures and supercritical fluids is the basis of this project. First, the design and fabrication of a Si/glass microreactor and its testing at high pressure and temperature conditions is addressed. A mechanical analysis and then fluid dynamic and thermal characterization of the two- and single-phase flow in the microreactor is performed. The solid catalyzed hydrogenation of cyclohexene serves as a model reaction to perform reaction studies on one hand and as comparison to macroscale reactors on the other hand. A high pressure three phase reaction (gas-liquid-solid) is conducted. Consequently, the phase boundary is eliminated by using scCO$_2$ as the reaction solvent and two phase reactions (SCF-solid) are performed in the microreactor. The main objectives of the thesis can be summarized as follows

- Design of a microreactor system, suitable for reactions in supercritical media
- Manufacture of a laboratory microreactor device including microfluidic connections
- Mechanical analysis of the microreactor device under high pressure reaction condition
- Systematic investigation of the effects of the operating parameters on the reaction performance and comparison with other systems.
Chapter 2

Fabrication

This chapter describes the design and fabrication of the microreactor for reactions under supercritical reaction conditions. Basics in microfabrication are listed and the choice for our reactor material is explained. The fabrication steps for the microreactor, the metallization and the microfluidic connections are given, where the detailed recipes for the processes are listed in Appendix A (p. 157). Different solid catalyst preparation methods for microreactors are presented.

2.1 Introduction into microfabrication

The ability to manufacture feature sizes in the range of $\mu m$ has opened a wide range of new possibilities in the area of chemical engineering and biology in the last years. The micromachining of silicon which had been developed for integrated circuits (IC) and microelectromechanical systems (MEMS) was adapted for microfluidic devices and used for the fabrication of microreactors. Standard processes such as photolithography, wet and dry etching, bonding and lift off processes are nowadays common tools for microreactor fabrication in silicon and glass. This fabrication method is relatively cost intensive, due to the need of a
2.2 Fabrication of Si/glass microreactors

When it comes to the fabrication of an efficient microreactor suitable for chemical reaction under supercritical conditions it is important to know the mechanical and thermal properties of its materials. The fabrication of such a reactor also depends on the materials micro-machinability.
Table 2.1 shows a comparison of materials used for micromachining purposes. \( \epsilon \) is the dielectric constant, \( E \) the Young’s modulus and \( \lambda \) the thermal conductivity.
Table 2.1: Comparison of micromachinable material for microreactors.

<table>
<thead>
<tr>
<th>Material</th>
<th>Costs</th>
<th>Fracture</th>
<th>Metallization</th>
<th>Machinability</th>
<th>$\epsilon$ [-]</th>
<th>$E$ [GPa]</th>
<th>$\lambda$ [$W m^{-1} K^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single crystal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>$$$$$$</td>
<td>brittle, strong</td>
<td>good</td>
<td>very good</td>
<td>11.8</td>
<td>165</td>
<td>156</td>
</tr>
<tr>
<td>Quartz</td>
<td>$$$$$$</td>
<td>brittle, strong</td>
<td>good</td>
<td>poor</td>
<td>4.4</td>
<td>87</td>
<td>7</td>
</tr>
<tr>
<td>GaAs</td>
<td>$$$$$$</td>
<td>brittle, fragile</td>
<td>good</td>
<td>poor</td>
<td>13.1</td>
<td>119</td>
<td>50</td>
</tr>
<tr>
<td>Sapphire</td>
<td>$$$$$$</td>
<td>brittle, strong</td>
<td>good</td>
<td>poor</td>
<td>9.4</td>
<td>490</td>
<td>40</td>
</tr>
<tr>
<td>Amorphous</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glass</td>
<td>$-$-$$$$$</td>
<td>brittle, fragile</td>
<td>good</td>
<td>fair</td>
<td>4.6</td>
<td>64</td>
<td>1.1</td>
</tr>
<tr>
<td>Fused Silica</td>
<td>$$$$-$$</td>
<td>brittle, fragile</td>
<td>good</td>
<td>poor</td>
<td>3.9</td>
<td>72</td>
<td>1.4</td>
</tr>
<tr>
<td>Plastic (PVC)</td>
<td>$$</td>
<td>tough, strong</td>
<td>poor</td>
<td>good</td>
<td>2.7</td>
<td>-</td>
<td>0.2</td>
</tr>
<tr>
<td>Cardboard</td>
<td>$$</td>
<td>tough, strong</td>
<td>poor</td>
<td>fair</td>
<td>3.5</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

(continued)
<table>
<thead>
<tr>
<th>Material</th>
<th>Costs</th>
<th>Fracture</th>
<th>Metallization</th>
<th>Machinability</th>
<th>$\epsilon$ [-]</th>
<th>$E$ [GPa]</th>
<th>$\lambda$ [$Wm^{-1}K^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>$-$$$$</td>
<td>brittle, strong</td>
<td>fair</td>
<td>poor</td>
<td>9.4</td>
<td>400</td>
<td>30</td>
</tr>
<tr>
<td>Aluminum</td>
<td>$$$</td>
<td>tough, strong</td>
<td>good</td>
<td>very good</td>
<td>-</td>
<td>77</td>
<td>240</td>
</tr>
<tr>
<td>Steel</td>
<td>$$</td>
<td>tough, strong</td>
<td>good</td>
<td>good</td>
<td>-</td>
<td>193</td>
<td>16.2</td>
</tr>
</tbody>
</table>

Table 2.1: Continued.
Silicon and aluminum provide a very good machinability in the micrometer size and show advantageous mechanical and thermal properties. The major difference between silicon and aluminum is their mechanical behavior and the micromachining methods. Since silicon shows a brittle behavior, its mechanical strength is statistically distributed and depends on the volume exposed to stress. Its major disadvantage is the non-existence of plasticity which would reduce stress peaks i.e. in sharp corners. The resistance to harsh chemical environment can be extended by a growing oxide or evaporate metallic layers on the surface. The main advantages of silicon are the outstanding micromachining techniques down to a submicron scale known from MEMS fabrication, usually performed in a cleanroom environment with plane Si wafers. Packaging and bonding to other materials i.e. glass offers a wide application for optical measurements in a reaction channel. Aluminum is micromachined with conventional improved techniques such as milling, turning, drilling, eroding and laser-machining to mention a few. Aluminum is not permeable to light and the chemical resistance is improved due to a passive oxide layer on the surface.

This project discusses in detail a reaction under supercritical condition in a microreactor. Due to this circumstance it is of major importance to have optical access to the reaction channel in order to understand the fundamental behavior of the phases under supercritical reaction conditions. Therefore we focus on silicon and glass as material for the microreactor. The choice is also influenced by the good thermal conductivity of Si which is of major importance by efficiently removing the heat during an exothermal reaction.

Silicon

Silicon was selected as material for the fabrication of a high pressure and high temperature microreactor for the following reasons:

(i) there is extensive knowledge about microfabrication techniques for silicon

(ii) the mechanical properties of single-crystal silicon is favorable for high pressure and high temperature applications and
(iii) its high thermal conductivity.

**Glass**

Glass is chosen for its optical transparency. Pyrex® (Corning, Corning, USA) and Borofloat® (Schott AG, Mainz, Germany) are borosilicate glasses with coefficients of thermal expansion which match the one of silicon. These types of glasses are used for highly stressed applications e.g. bullet proof glass and inspection glass in chemical reactors. With an anodic bonding process the glass can be permanently attached to the silicon surface.

### 2.2.2 Fabrication process of high pressure microreactors

The detailed fabrication process described in this section is shown in Fig. 2.2.

Photolithography, dry etching and anodic bonding techniques are used for the manufacturing in a cleanroom environment. The most important fabrication steps are explained in more detail.

The Si wafer is covered with a positive photoresist and patterned by UV light with a high resolution mask containing the microfluidic channel structure (Fig. 2.2(A)). (B) shows the developed photoresist on the Si wafer. (C) The dry etching of the channel structures is performed using an Inductive Coupled Plasma (ICP) etching system. The etching is explained in more detail in Section 2.2.2. An optional step shows (D) where a layer of nobel metal is evaporated onto the channel walls by physical vapor deposition (PVD). The Titanium layer acts as undercoating where the Palladium is the catalytically active surface. Other metallic layers such as Nickel can also be used as protection against harsh chemicals (de Mas et al., 2003). The microfluidic connections are established from the backside of the Si wafer. For this reason the wafer is cleaned and steps (A) - (C) are repeated. (E) shows the fully etched Si wafer with the channel structures and the inlets and outlets at the backside of the
2.2 Fabrication of Si/glass microreactors

Subsequently an anodic bonding step is performed to hermetically cover the microfluidic channels in the Si with glass. This step forms the actual microreactor (F).

Six microreactors can be fabricated simultaneously on one wafer. Therefore the Si/glass composite device is cut with a dicing saw to obtain microreactor chips of a corresponding size of $18 \times 46 \, \text{mm}^2$. A metal deposition around the inlets and outlets (G) guarantees wetting of the Si surface by solder. Subsequently, stainless steel capillaries are soldered onto the reactor as microfluidic connections. As this microfluidic connections are a key feature of a high pressure microreactor we focus more on this step in section 2.3.

Mask resolution

The photolithographic mask is a printed transparent foil which is placed on a glass substrate holder. The printer has a resolution of 2400 dpi. This results in a step resolution of $10.58 \, \mu m$. This is in good agreement
with the steps seen in diminutions of channelwidths. Usually three lines are necessary to get a reasonable resolution for stand alone features. This leads to a minimum size of $32 \mu m$. The minimal feature size used in the fabrication process is $50 \mu m$.

### Etching

A deep reactive ion etching (DRIE) is used to anisotropically etch the Si. The main advantage of this technique is the possibility of manufacturing high aspect ratio channels and the rectangular shape of the etched channel. The etching is performed after the Bosch advanced silicon etch (ASE) technique (Laermer and Schilp, 1996). This method uses alternating etch and passivation cycles. This results in a vertically etched channel wall. The reactions involved in the cycles are

$$Si + 4F^- \rightarrow SiF_4 \quad \text{etch cycle} \quad (2.1)$$

$$SF_6 + e^- \rightarrow SF_5^+ + F + 2e^- \quad \text{passivation cycle.} \quad (2.2)$$

The different process gases are fed into the etching chamber according to the cycles. An inductively coupled plasma (ICP) forms the reactive species. The etching can be divided into a chemical part which follows the reaction equation 2.1 and etches the silicon isotropically. An additional physical etching with accelerated electrons is performed by hitting the Si surface and release Si Atoms. This etch type acts anisotropically. Different etch characteristics can be achieved by varying electric and magnetic field power.

Fig. 2.3(a) shows a cross section through an etched Si channel closed with glass. We see a slightly concave shape of the channel bottom. The reason for this phenomenon is a decreased etch speed close to the wall. Fig. 2.3(b) depicts a scalloping effect at the channel wall. This is in the nature of the Bosch process and indicates the depth of one single etch cycle. Given the parameter settings of this project the depth per cycle is within the range of $1.5 \mu m \ cycle^{-1}$ and the average surface roughness is $0.15 \mu m$ (peak-to-valley).
2.2 Fabrication of Si/glass microreactors

2.2.3 Microfluidic packaging

Several aspects play an important role for the direct bonding of two surfaces into a mechanically stable composite that suits high pressure microreactors:

- Cleanliness (chemical surface state). Intense cleaning procedures have to be carried out.

- Shape (geometrical surface state). Wafers in wafer bonding are flat and relatively thin. Therefore, the flatness (when placed on a vacuum chuck) is rather determined by the parallelism of wafer than by its flatness.

- Roughness/smoothness (mechanical surface state). Van der Waals forces, responsible for direct bonding are relatively weak forces (1/10 of a covalent bond). These forces are a function of the mutual distance between the surfaces that ought to be bonded. The root-mean-square-value has to be between 0.5 - 2 nm.

- Quality of material (physical perfection). Usually prime quality Si wafers were contaminated with less than 10 particles larger than 0.3 µm.

**Figure 2.3:** Scanning electron micrographs of dry etched Si processed in an ICP. (a) Cross section through the microfluidic channel covered with glass. (b) Scalloping effect due to the cycled etch process at the channel wall.
(Schmidt, 1998) provides an overview over existing wafer-to-wafer bonding techniques.

**Anodic bonding**

Anodic bonding, also known as field-assisted thermal bonding is the method applied in this project to cover the microfluidic channel with a glass wafer. This provides a hermetic and mechanically stable chemical bond between the two substrates. Typically, a sodium-rich glass wafer and a silicon wafer perform the bond. It is also possible to bond two silicon wafers with a sputtered glass layer (typically $\sim 4 \, \mu m$). Thus, at least one of the two to-be-bonded surfaces has to contain an electric field drivable component or element.

In principal the contacted wafer pair is heated up close to the glass-softening point ($300 - 450 \, ^\circ C$). The bond is completed by applying an electric field with a voltage of $200 - 1500 \, V$ for glass-silicon wafer bond and $50 \, V$ for silicon-silicon wafer bond with sputtered glass layer. The actual bond process is not fully understood yet. It is suggested that $Na^+$ ions drift towards the cathode at elevated temperature under the applied voltage. The fixed negative charge in the glass creates a high electric field across the bond interface with image charges in the silicon. Consequently the wafers are pulled together. The large electrical field transports the oxygen into the glass to the silicon-glass interface, the silicon oxidizes and a thin $SiO_2$ layer creates the bond.

Fig. 2.4 shows a scheme of the anodic bonding of glass to Si. In the presented fabrication process the temperature is $450 \, ^\circ C$ and the applied voltage is $1500 \, V$. Additionally, the 100 $mm$ diameter wafers are compressed with a force of $90 \, N$ to increase the bonding strength at the interface. This is important for the operation of the microreactors at high pressure. The bond process is over when no moving ions are observable and hence no current is detectable, normally after approximately 20 $min$.

As in every composite of different materials with different coefficients of thermal expansion (CTE), thermomechanical stress occurs by applying a temperature difference. Both glass and Si are brittle materials and should therefore not sustain high strain. Their CTE have therefore to
match as well as possible over a wide range of temperature in order to minimize thermal stress in the composite after the cooling down from process temperature. Fig. 2.5 shows the different CTE of Si, Pyrex® and Borofloat® as well as Kovar® - a Ni-Co alloy - as a comparison. This material was especially developed to match the low CTE of Si.

**Figure 2.4:** Anodic bonding of Si and glass. Scheme of the anodic bonding process.

**Figure 2.5:** CTE of Si, glass and Kovar.
2.3 Microfluidic connections

2.3.1 Introduction

The fluid delivery system of a microreactor usually consists of macroscopic equipment like pumps and pressure vessels, while the microreactor itself has microscopic dimensions. This means that the ”microworld” of a microreactor has to be connected with its macroscopic outside environment. In this project the microreactor and its microfluidic connections must satisfy high demands in terms of mechanical, thermal and chemical stability. The microfluidic connections turn out to be a main challenge when designing a high pressure and high temperature microreactor. The term ”microfluidic connection” refers to all connections that are external to the microreactor device and are necessary for the microreactors operation and testing. They include microfluidic connections for gas, liquid or gas-liquid mixtures and catalyst particle inlet/outlet.

The connections must fulfill the following requirements:

- Gas-tightness
- Temperature resistant over 80 °C
- Pressure resistant up to 140 bar
- Reliability in manufacturing
- Resilient to handling loads
- Protection of the device from handling loads.

There are several ways of connecting a microreactor to the outside world, e.g. using solder, epoxy, braze, glass and press fittings.

2.3.2 Review of microfluidic connections

There exist a variety of different microfluidic devices for many applications. Each of these devices offers a unique way to connect the
microdevice with its surrounding experimental setup. Up to present, a huge number of different systems exist to connect the macroscale environment (pumps, valves, analyzing apparatus) to a microreactor. These microfluidic connections are mainly used in research and are not yet standardized. This chapter presents an overview of microfluidic interconnects focused on silicon-based microreactors. The field of biological application in microfluidic systems (mainly linked to micro total analysis system (µTAS) or lab-on-a-chip) is not discussed in detail, since these devices are not fabricated for high pressure and temperature.

Two major methods exist for applying microfluidic connections on Si/glass chips at elevated temperature and pressure: (1) integrated connections and (2) modular connections (Fredrickson and Fan, 2004).

**Integrated microfluidic connections**

Integrated connections are permanently attached and are used for pressure and vacuum applications. Major disadvantages are the complicated fabrication and the dead volume, which is not easily assessable.

**Table 2.2:** Selected publications of integrated microfluidic connections. n.s. = not specified.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Method</th>
<th>Reactor material</th>
<th>Connection material</th>
<th>$p_{\text{max}}$</th>
<th>$T_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bings et al.</td>
<td>flat drilled holes, glued</td>
<td>glass</td>
<td>fused silica</td>
<td>n.s.</td>
<td>n.s.</td>
</tr>
<tr>
<td>(1999)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gray et al.</td>
<td>etched holes, press fitting</td>
<td>Si/glass</td>
<td>plastic coupler</td>
<td>34 bar</td>
<td>n.s.</td>
</tr>
<tr>
<td>(1999)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Puntambekar and Ahn</td>
<td>flanged tubing</td>
<td>glass</td>
<td>PEEK</td>
<td>66 bar</td>
<td>n.s.</td>
</tr>
<tr>
<td>(2002)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(continued)
Table 2.2: Continued.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Method</th>
<th>Reactor material</th>
<th>Connection material</th>
<th>( p_{max} )</th>
<th>( T_{max} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pattekar and Kothare (2003)</td>
<td>directly glued</td>
<td>Si/glass</td>
<td>Teflon</td>
<td>21 bar</td>
<td>275 °C (at ( p_{amb} ))</td>
</tr>
<tr>
<td>Gonzalez et al. (1998)</td>
<td>horizontally inserted tube</td>
<td>Si</td>
<td>rubber</td>
<td>1.37 bar</td>
<td>n.s.</td>
</tr>
<tr>
<td>Spiering et al. (1997)</td>
<td>directly glued</td>
<td>Si/glass</td>
<td>metal, glass</td>
<td>137 bar</td>
<td>n.s.</td>
</tr>
<tr>
<td>Lee et al. (2004)</td>
<td>plastic screws</td>
<td>glass</td>
<td>tubing</td>
<td>1.2 bar</td>
<td>n.s.</td>
</tr>
<tr>
<td>Tsai and Lin (2001)</td>
<td>directly glued</td>
<td>Si/glass</td>
<td>Mylar</td>
<td>1.9 bar</td>
<td>n.s.</td>
</tr>
<tr>
<td>Peles et al. (2004)</td>
<td>Kovar glass sealing</td>
<td>Si</td>
<td>Kovar</td>
<td>125 bar</td>
<td>1300 °C</td>
</tr>
<tr>
<td>Blom et al. (2001a)</td>
<td>Kovar anodic bonding</td>
<td>Si/glass</td>
<td>Kovar</td>
<td>200 bar</td>
<td>250 °C</td>
</tr>
<tr>
<td>Trachsel et al. (2006)</td>
<td>soldering</td>
<td>Si/glass</td>
<td>stainless steel</td>
<td>140 bar</td>
<td>80 °C</td>
</tr>
<tr>
<td>Murphy et al. (2007)</td>
<td>soldering</td>
<td>Si/glass</td>
<td>stainless steel</td>
<td>200 bar</td>
<td>n.s.</td>
</tr>
</tbody>
</table>

Tab. 2.2 shows different published integrated microfluidic connections. We conclude that only a few applications are suitable for high pressure. The combination of high pressure and high temperature is very rarely
2.3 Microfluidic connections

reported. The work of (Peles et al., 2004) uses the glass sealing of Kovar tubings onto a Si device. The glass melts at high temperatures and forms a hermetic seal around the positioned tubings. All chosen materials show little difference in CTE. Problems in quality variation due to cavity formation during the process are reported.

The connection quality realized by anodically bonding Kovar alloy onto the glass surface reported in (Blom et al., 2001a) is very sensitive to the surface roughness of the contacting material. The values for $p_{\text{max}}$ and $T_{\text{max}}$ given in the article are derived from tensile tests and the bond temperature and not verified experimentally.

Modular microfluidic connections

Modular connections consist of reusable parts. A housing in which the microreactor is embedded and compressed provides leak tight connections. A precise alignment of the connecting components is necessary.

Table 2.3: Selected publications of modular microfluidic connections

<table>
<thead>
<tr>
<th>Reference</th>
<th>Method</th>
<th>Reactor material</th>
<th>Sealing material</th>
<th>$p_{\text{max}}$</th>
<th>$T_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nittis et al. (2001)</td>
<td>PEEK housing</td>
<td>Si/glass</td>
<td>Elastomer</td>
<td>6 bar</td>
<td>n.s.</td>
</tr>
<tr>
<td>Yao et al. (2000)</td>
<td>O-ring</td>
<td>polyolefine</td>
<td></td>
<td>5.5 bar</td>
<td>n.s.</td>
</tr>
</tbody>
</table>

Tab. 2.3 shows that only low pressure ranges can be achieved with mod-
ular connections. The main reason is the press fitting which forms the seal between the microreactor and the housing. There, only limited mechanical pressure can be applied so that the microreactor chip does not break due to non symmetric stress distributions in the housing. In Tab. 2.4 commercial microfluidic connections are listed, with the corresponding operating range.

**Commercial microfluidic connections**

<table>
<thead>
<tr>
<th>Reference</th>
<th>Method</th>
<th>Reactor material</th>
<th>Sealing material</th>
<th>$p_{max}$</th>
<th>$T_{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Müller et al. (2005)</td>
<td>Backbone system</td>
<td>variable</td>
<td>i.e. Viton</td>
<td>100 bar</td>
<td>300 °C</td>
</tr>
<tr>
<td>Upchurch, Inc.</td>
<td>NanoPort</td>
<td>variable</td>
<td>adhesive rings</td>
<td>103 bar</td>
<td>n.s.</td>
</tr>
<tr>
<td>Bayer (2000)</td>
<td>welded housing</td>
<td>etched Inconel</td>
<td>welded</td>
<td>50 bar</td>
<td>700 °C</td>
</tr>
<tr>
<td>IMM, Mainz, Germany</td>
<td>housing</td>
<td>stainless steel</td>
<td>n.s.</td>
<td>600 bar</td>
<td>500 °C</td>
</tr>
<tr>
<td>(Kestenbaum et al., 2002)</td>
<td>screwed housing</td>
<td>etched stainless steel</td>
<td>50 bar</td>
<td>500 °C</td>
<td></td>
</tr>
<tr>
<td>(Löbbecke et al., 2005)</td>
<td>FAMOS</td>
<td>variable</td>
<td>n.s.</td>
<td>150 °C</td>
<td></td>
</tr>
</tbody>
</table>

(continued)
2.3 Microfluidic connections

<table>
<thead>
<tr>
<th>Reference</th>
<th>Method</th>
<th>Reactor material</th>
<th>Sealing material</th>
<th>$p_{max}$</th>
<th>$T_{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taghavi-Moghadam et al. (2001)</td>
<td>CYTOS</td>
<td>stainless steel</td>
<td>Kalrez, Viton</td>
<td>6 bar</td>
<td>200 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td>plates</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Siemens</td>
<td>SIPROCESS</td>
<td>stainless steel</td>
<td></td>
<td>15 bar</td>
<td>150 °C</td>
</tr>
</tbody>
</table>

2.3.3 Fabrication of high pressure microfluidic connections

The literature in the previous section shows that integrated microfluidic connections have a higher potential for high pressure and high temperature application like they are necessary for this project. We therefore decide to solder capillaries onto the microreactor chip. Using metallic solder is preferable as the connecting material between the capillary and microreactor chip compared to epoxy or glass. Epoxy adhesives are easy to handle and the application only needs cleaned surfaces. The main drawbacks are the limited chemical resistance to harsh chemicals and the limited mechanical strength at temperatures above 70 °C. Experiments using high strength construction adhesive DP 490 (Scotch-Weld, 3M Schweiz, Rüschlikon, Switzerland) failed at temperatures above 70 °C combined with pressures over 100 bar (test fluid: water).

Glass as the connecting material would fulfill the requirements regarding high mechanical strength and chemical resistance. The possibility to easily match the CTE of all involved materials makes this method favorable for high temperature applications like in microengines and microrockets. The disadvantage is the demanding fabrication process at temperatures above the melting point of glass. In the case of (Peles et al., 2004) the process temperature is 1038 °C. This is far above
the process temperature of anodic bonding and can not be applied to Si/glass microreactors. A comparable method to glass sealing is the use of low-temperature sealing glass instead of glass. These glasses usually contain lead and have process temperatures in the range of \( T = 350 - 500 \, ^\circ C \). As organic binders degas during processing, a vacuum oven is necessary. The forming of voids during fabrication is an additional problem. This plays a demanding role for glass processing.

Metallic solder is chosen as connection material, since the process temperature is in the range of 200 \(^\circ C\) and the mismatch of the materials’ CTEs can be kept at a minimum. In the following section the fabrication of metallic soldered connections onto a Si/glass microreactor chip is described.

Chromium, nickel, copper and gold were deposited around the inlet and outlet holes according to Fig. 2.6(a). The evaporation process involves local heating of a target material to generate a vapor that condenses on a substrate surface. Target heating is accomplished either resistively or by scanning an electron beam over the target. Resistance heating is easy to realize but it can result in spreading impurities present in the filament. It is also limited in the evaporated film thickness by the small size. In our case we used electron beam evaporation (Pfeiffer Vacuum Classic 500). Electron beam evaporation can provide better quality and higher deposition rate (50 - 500 nm/min) but it is a much more complex process. Therefore a water cooled target and shielding from X-rays, that are generated when the energetic electrons strike the target, is needed.

An aluminum shadow mask is used during the evaporative deposition. 50 \( nm \) gold is used as the top layer to provide complete wetting with the tin-silver based solder. 300 \( nm \) copper prevents the formation of an oxide layer on the nickel layer. 100 \( nm \) nickel itself acts as a diffusion barrier. 10 \( nm \) chromium is the actual undercoating on the silicon surface. The layer thickness is measured during the process by an oscillating crystal and has an accuracy of approximately 10%.

Stainless steel capillaries of 50 \( mm \) length (o.d. = 1.59 \( mm \), i.d. = 0.5 \( mm \)) are turned on one end to provide a slight cone for accurate positioning on the etched inlet and outlet holes. About 8 \( mm \) at the end
of the tubing is ground to remove the oxide layer. After grinding, the capillary is cleaned with acetone and immediately pre-tin-plated with the corresponding flux agent for stainless steels.

The soldering setup consists of a hot plate and a positioning table. Capillaries are mounted on a drill chuck for precise orthogonal alignment on the microreactor chip. A hot plate \((T = 160 \, ^\circ C)\) and a soldering iron \((T = 350 \, ^\circ C)\) for local heating are used for heating the parts and melting of the solder. Prior to soldering, the capillaries are tinned with flux agent. See Appendix A (p. 157) for further details. No plugging of the channel due to flux or solder was observed during fabrication. Fig. 2.6(b) shows a schematic of the soldered microfluidic connection.

**Figure 2.6:** Scheme of the microfluidic connection fabrication. (a) Thin film metallization using an alumina shadow mask and electron beam evaporation. (b) Soldered capillary on the backside of the Si/glass microreactor.

### 2.4 Integrated heating

The small thermal mass and the high heat conductivity of Si makes the microreactor suitable for integrated resistive heating. An additional photolithographic and evaporation step is necessary to pattern the backside of the microreactor with platinum heating and resistance thermometers.
Appendix A (p. 157) provides a description of the detailed lift off process. Fig. 2.7 shows a photograph of the backside of microreactor with two combined resistive heating and resistance thermometer elements as well as the metallic soldering pads around the inlets and outlets. The enlarged view shows the meandering structure of the heating with a width of 100 \( \mu m \) and the resistance thermometer (width = 50 \( \mu m \)). A chromium layer is used as adhesion layer whereas the functional layer consists of 200 \( nm \) platinum. The electrical resistance is

\[
R = \frac{\rho_{Pt} L}{A} \tag{2.3}
\]

with \( \rho_{Pt} \) the electrical resistivity of platinum (\(= 105 \, n\Omega m\)), \( L \) the length and \( A \) the cross section of the evaporated area. The resistive heating and the resistance thermometer have an electrical resistance of 180 \( \Omega \) and 100 \( \Omega \), respectively.

**Figure 2.7:** Photograph of an evaporated resistive heating and resistance thermometer on a Si/glass microreactor.

### 2.5 Catalyst support

Different methods exist to incorporate a solid catalyst in a chip microreactor.
2.5 Catalyst support

- Microreactor material itself is catalyst
- Porous catalyst carrier
- Wire in channel
- Thin film at channel wall
- Packed bed.

When the microreactor material itself is the active catalyst, the catalyst surface is relatively low but can easily be calculated from the channel geometry (Fichtner et al., 2001; Kestenbaum et al., 2002). The most common method for a porous catalyst carrier surface inside a microreactor is the washcoat technique (Srinivas et al., 2004) followed by impregnation with the corresponding catalyst. Other methods are the sol-gel method (Haas-Santo et al., 2001) and the use of porous silicon electrochemically fabricated in a hydrofluoric acid (HF) ethanol solution (Laurell et al., 1996). One advantage of such systems is the high surface area of such porous layer on the channel walls. The drawbacks are the difficult characterization of surface area of catalyst loading and the lack of exchangeability (Veser et al., 2000) presented a simple method for a catalyst in a microreactor. A catalytically active wire is inserted in a microchannel which additionally can be used as resistive heating. A thin catalytic active metal film at the channel wall is easy to obtain, when working in a cleanroom. Optical access into the reaction channel in case of a Si/glass microreactor and the ease of calculation of the surface area are other advantages to be mentioned. The main drawbacks of thin films are the small surface area as they are not porous and the impossibility of exchange in the case of deactivation of the catalyst. The manufacturing of thin metallic layers can be done by sputtering, PVD or CVD. In the case of high aspect ratios shadowing effects from the channel edges have to be taken into account. In a first approach we directly evaporated Pd catalyst on the microchannels before the anodic bonding of the Si wafer. 25 nm of titanium, which acts as an undercoating, and 60 nm of palladium as active catalyst are evaporated with electron beam evaporation (Blazers BAK600). The catalytically
active surface of the reactor can be approximated with the etched surface in the Si wafer. Fig. 2.8(a) shows the metallic layer at a vertical channel wall with the typical scalloping shape from the dry etch process. A shadowing region with no metal layer occurs near the scallop. Fig. 2.8(b) shows a more homogeneous layer at the channel bottom. Compared to the layer at the channel wall its thickness is increased due to the better exposition in the evaporation process.

Figure 2.8: Scanning electron micrographs of the catalyst surface in an own manufactured microreactor. (a) Evaporated Pd catalyst with a Ti undercoating on silicon on the vertical wall and (b) on the bottom of the etched microchannel.

Experimental studies in our laboratory of the gas-liquid hydrogenation of cyclohexene using evaporated Pd on the channel walls as catalyst showed no conversion for different reaction conditions. This leads to the conclusion that the catalytic surface is too small to reach measurable conversion in the case of a gas-liquid reaction system. It is also possible that, during the anodic bonding process, the metal oxidizes or transforms at the high temperature and voltage exposed and this leads to a deactivation of the metallic layer. In the gas phase the same reaction could be performed with sputtered Pt as catalyst on the channel walls (Besser et al., 2003). This would favor the conclusion of a too small catalyst surface since the mass transport in the gas phase is drastically increased compared to the gas-liquid phase case. (Losey et al., 2001, 2002) use a packed bed microreactor for the characterization of mixing and mass transfer of multiphase reactions. Since the analysis of such reactions is within the scope of this thesis we choose
a microfabricated packed bed as catalyst support because of following reasons:

(1) comparable with macroscale reactors due to the use of standard catalyst
(2) substitution of catalyst possible
(3) measurable properties by standard techniques
(4) high and well defined catalyst surface area
(5) optical access into the reaction channel
(6) enhanced heat removal compared to empty microchannels (Jiang et al., 2001).

The disadvantages are the high pressure drop and the non-ideal particle to hydraulic diameter ratio \((d_p/d_h)\). The following section describes the packed bed microreactor in detail.

### 2.5.1 Packed bed

**Catalyst**

The catalyst used is Pd on alumina \(\left(\text{Al}_2\text{O}_3\right)\) particles (Johnson Matthey, 2 wt\% Pd, Typ 31, Product code: 113031) which is commercially available. The metal surface to mass ratio is 1.75 \(m^2g^{-1}\) and the dispersion is 19.7 % measured with pulsed CO chemisorption (Autochem 2910, Micromeritics, Mönchengladbach, Germany). The BET surface is 157.7 \(\pm 1.3\) \(m^2g^{-1}\) (Tristar3000, Micromeritics).

The particles are dispersed in distilled water and sieved in an ultrasonic bath for 30 \textit{min} to obtain a well defined particle size distribution. The stainless steel sieve has a meshsize of 50 \(\mu m\) where the larger fraction of particles are used. Particle size distribution are measured using laser diffraction spectroscopy (HELOS, Sympatec GmbH, Clausthal-Zellerfeld, Germany).
The ideal particle size is a trade off between the handling of the particles in the microchannel, the pressure drop and homogeneity of the packed bed.

While smaller particles are easy to insert and lead to a more homogeneous packed bed in terms of spatial void fraction distribution, the pressure drop increases drastically according to the Ergun equation for a constant particle size (Ergun, 1952):

\[
\frac{\Delta p}{L} = f_p \cdot \frac{\rho u_0^2}{d_p} \cdot \frac{1 - \epsilon}{\epsilon^3}
\]

(2.4)

\[
f_p = \frac{150}{Re_p} + 1.75
\]

(2.5)

\[
Re_p = \frac{d_p u_0 \rho}{\eta}
\]

(2.6)

where \( \Delta p \) is the pressure drop across the bed, \( L \) the length of the bed, \( d_p \) the particle diameter, \( \rho \) the fluid density, \( \eta \) the dynamic viscosity of the fluid, \( u_0 \) the superficial velocity in the empty channel and \( \epsilon \) the void fraction of the bed.

The porosity of the packed bed is calculated from the catalyst weight in the microreactor, the reactor volume and the catalyst particle porosity (\( \epsilon_{cat} = 0.72 \), calculated from the pore distribution values from the supplier) and is \( \epsilon_{pb} = 0.69 \). The weight of the catalyst could be measured with an accuracy of \( \pm 0.05 \ mg \) on a precision balance (AT400, Mettler, Switzerland). The apparent density of the catalyst is \( \rho_{app} = 1120 \ kgm^{-3} \). Fig. 2.9 shows an image of the packed bed inside a microreactor.

Fig. 2.10(a) shows the particle size distribution of a Pd on carbon catalyst without sieving (Product 75992, Sigma-Aldrich, Buchs, Switzerland). The graph indicates that carbon as catalyst support tends to have a large agglomeration potential, since smaller particles appear after an ultrasonic treatment. The dry sieving also proves this conclusion. Different sieve sizes did not show any significant selection. This agglomeration of particles is critical for microchannels since it blocks the microchannel. Additionally, the formation of smaller particles due to the
small mechanical stability of carbon leads to agglomeration even after sieving.

Fig. 2.10(b) shows sieved Pd on alumina particles. It shows a well defined size distribution with a mean diameter of $x_{50} = 115 \mu m$. We use this catalyst and sieving procedure to form the packed bed in the microreactor since the particles are of well defined dimensions and the spherical shape reduces the danger of agglomeration and clogging.

The particles are inserted in the microchannel in a water suspension applying vacuum at the outlet. Ultrasonic treatment ensures a homogeneous particle distribution in the microchannel. After the reaction the catalyst particles are removed by pressurized air and ultrasonic agitation. An oxygen plasma treatment for 3 min removes all possible organic residuals in the packed bed and facilitates the exchange of catalyst.

2.6 Conclusions and summary

High pressure resistance and the need for optical access into the reaction channel for in situ measurements lead to the fabrication of a chip based Si/glass microreactor. The ability to withstand high mechanical stress implies a proper choice of the materials and a precise microfabrication of the device. Photolithography, dry etching and anodic bonding is chosen
2. Fabrication

Figure 2.10: Particle size distributions of two different catalyst supports. (a) Pd on carbon particles as delivered from supplier with and without ultrasonic treatment. The suppliers data is also shown. (b) Retained Pd on $\text{Al}_2\text{O}_3$ particles after sieving with a mesh size of 50 $\mu$m in an ultrasonic water bath.

to manufacture the microreactor. Appendix A (p. 157) explains the detailed procedures of the fabrication in the cleanroom. Special attention is paid on the microfluidic connections — the interface between the macro- and micro-environment. Different methods for microfluidic connections and materials are reviewed. Metallic solder as joint material for the attachment of capillaries onto the microfluidic chip turns out to be suitable for the specified operating conditions of 140 bar and 80 °C and is easy to manufacture. Different metallic layers are evaporated around the inlet and outlet holes in order to make the Si surface wettable for solder.

To follow the idea of an integrated microreaction system fabrication of an integrated resistive heating and resistance thermometer is shown. For conducting chemical reactions in the microreactor different catalyst incorporation methods are given. A packed bed is chosen as catalyst support for several reasons, among others: the optical transparency allows the online analysis of reactive species in the catalyst bed, well defined commercial catalyst particles can be used and the catalyst can be exchanged.

The final design of the microreactor for reactions using $\text{scCO}_2$ as reaction solvent consists of an optically transparent Si/glass chip with soldered
2.6 Conclusions and summary

capillaries as microfluidic connections. The fluids are brought in contact and mixed on chip. Catalyst particles are inserted into the microreactor and provide a well defined reaction section.
A microreactor which is suitable to conduct a reaction in \( scCO_2 \) has to withstand pressure in the range of 140 \textit{bar} and temperatures around 80 \( ^\circ\)C. A detailed mechanical characterization of the microreactor checks whether the fabrication techniques suit this specifications. This chapter presents the experimental results of tensile and pressure tests for the microfluidic connections and an analytical approach for the mechanical stability studies of a pressurized microchannel.

Tensile tests are conducted to simulate the loads on the fluidic connection due to pressure in the microreactor and due to handling. Tensile tests do not exactly represent the loads from high pressure because the boundary conditions and failure modes are not identical. Therefore tensile tests are limited when representing the actual load case on the microfluidic connections. The microreactor is considered to fail as soon as the first leak appears. Leaks cannot be detected by tensile tests but by the separation of the capillary from the device. However, these tests provide a basis for the maximal strength of the fluidic connection and offer the possibility to quantitatively compare different designs and fabrication techniques. Furthermore, pressure and leak tests are carried
out. The microreactor is filled with water pressurized with nitrogen and placed in a heated water bath to test it under pressure and thermal load conditions. Also helium leaktests are conducted to confirm the hermetic seal of the bonding and the microfluidic connections.

### 3.1 Experimental

The tensile test specimens consist of a Si/glass piece with the size of \( \sim 10 \times 10 \text{ mm}^2 \) with a soldered capillary as described in chapter 2.3. The specimens are fixed in a holder device that provides a transmission of force from the capillary to the soldered part of the connection. A wedge gripping device applies the tension on the capillary as shown in Fig. 3.1. Alignment is checked before each test run and adjusted by moving the specimen in the holder. The holder itself is not completely fixed so that the specimen can move and no moment is introduced on the specimen.

The experiments are carried out on a tensile test machine (Zwick 1474, Zwick, Ulm, Germany) with a testing temperature range of 5 - 300°C and a relative accuracy of ±0.5% at 200 N. To conduct tensile tests at elevated temperatures, a climate chamber is installed around the testing section of the machine. The equipment is heated up for 30 min to ensure uniform temperature. The climate chamber is stabilized for 5 min after loading the specimen.

All experiments are performed with a pre-load of 2 N and a test speed of 1 mm min\(^{-1}\). The experiment was terminated when the capillary was separated from the silicon surface.

Helium leak tests were carried out with a He-leak tester (ASM 142, Alcatel). For pressure test, the microreactor was filled with water, placed in a heated bath and pressurized with nitrogen.
3.2 Results tensile tests

Fig 3.2 shows a typical path-force diagram. Connections with 4 mm soldered diameter have higher maximum force than the ones with 6 mm. Since all specimens have failed with the pull out of the capillary, the influence of the pad size has a minor importance. Therefore we decide to use a pad diameter of 5 mm for future fabrications. This means a trade off between smaller normal tensile stress on the connection (larger size) and less space consumption on the chip (smaller size). The large variation in maximum force indicates that different failure mechanisms occur and have to be considered.

The maximum force $F_N$ indicates the value of the tensile load at which capillary and device separate. Considering a simplified device-solder-capillary connection, one can calculate a theoretical value for the maximum pressure in the microreactor for which the connection is suitable. Fig. 3.3 shows the schematic force balance of a pressurized microfluidic connection soldered on a Si chip, assuming no moments.
3.2 Results tensile tests

Figure 3.2: Typical path-force diagram of tensile specimens with different diameter of the evaporated pads $d$.

applied on the specimen by the holder. The force balances in Eq. 3.1 lead to a maximum theoretical pressure $p_{i,max}$ which can be derived from tensile tests.

$$\int \int p_i \cdot r \partial \varphi \partial z = 0 \quad \text{r-direction} \quad (3.1)$$

$$\int \int p_i \cdot r \partial \varphi \partial r = F_N \quad \text{z-direction} \quad (3.2)$$

The exact value of the pressurized area in z-direction $A_p$ in Fig. 3.3(a) is unknown due to positioning uncertainties of the capillary. Therefore we use the outer diameter of the capillary ($d_c = 1.59 \ mm$) to conservatively calculate maximum pressure. The maximum pressure can be calculated
Figure 3.3: Schematic pressure distribution in the fluidic connection and the corresponding cut free sketch. (a) The inner radius \( r_a \) of the capillary is smaller than the etched radius in the silicon \( r_b \), \( r_a < r_b \). (b) By using larger inner diameters of the capillary (i.e. for catalyst inlet/outlet) is \( r_a > r_b \).
with the outer diameter of the capillary from:

\[
p_{i,max} = \frac{F_N}{A_p} = \frac{F_N}{\pi d_c^2/4}. \tag{3.3}
\]

There are three different failure types which occurred during the tensile tests. Fig. 3.4 shows photographs of the typical failure types.

**Figure 3.4:** Photographs of the three typical failure modes. (a) Failure type 1, separation of capillary from solder. (b) Failure type 2, separation of the Cr undercoating from Si. (c) Failure type 3, fracture of the Si/glass specimen.

**Failure type 1**

Separation of the capillary from the solder occurs when the shear stress in the interface between the capillary and the solder is higher than the maximum value. An approximation of the shear stress in this interface can be determined by dividing the maximum tensile force by the area on the shell of the capillary covered by solder. As the length of the capillary covered by solder is in the order of 1 mm this area is about 5 mm\(^2\). The lowest measured tensile force for failure type 1 was 153 N, which results in a minimum shear stress of about 30 MPa. This is in the range of the minimum shear strength of solder on stainless steel of 25 MPa provided by the supplier. 25 MPa of shear stress on the wetted area on the capillary results in a total tensile force of 125 N. This would lead to a theoretical maximum pressure of 629 bar on the connection.
Failure type 2

Failure type 2 is the separation of the chromium layer from the silicon surface. The normal stress between the chromium layer and the silicon surface leads to failure. The normal stress is calculated by dividing the tensile load by the chromium surface area \(A = \pi d^2/4 = 19.63 \text{ mm}^2\) with \(d = 5 \text{ mm}\) being the diameter of the evaporated pad. The lowest measured tensile force before failure was 210 \(N\) \((p_{i,\text{max}} = 1045 \text{ bar})\), which results in a maximum normal stress of 10.7 \(\text{MPa}\) for the undercoating. It is evident that this failure type is strongly dependent on the cleaning of the silicon surface before the evaporation.

Failure type 3

The fracture of the Si/glass composite reaches the highest values for tensile loads. The stress situation is much more complex than in the former two failure types. The sample holder and its geometry play an important role in the stress distribution around the soldered connection. The holder applies shear stress onto the sample and the Si/glass undergoes brittle failure. This indicates a higher mechanical strength of the connection than the Si/glass composite. For this failure type, no information about the mechanical strength of the connection can be derived; but conclusions about maximum handling loads which can be applied to the microreactor are possible.

The data in Fig. 3.5 shows the three series of tensile tests at different temperatures. A large variation in all series and a slight decrease in maximum load with increasing temperature can be seen. The large variation of failure load, especially for failure type 3, is explained by the brittle behavior of silicon and glass. This behavior leads to a statistically distributed mechanical strength represented by a Weibull distribution (Weibull, 1951) in Eq. 3.4

\[
P_f = 1 - exp\left(\frac{R_m}{R_{m0}}\right)^m
\]  

(3.4)
3.2 Results tensile tests

Figure 3.5: Measured tensile loads of three series at different temperatures.

where $P_f$ is the probability of failure, $R_{m0}$ the reference load where 63.2% of the specimens fail and $m$ is the reliability, which is improved for higher values of $m$. A 1% probability of failure was calculated at a tensile load of $R_m = 91.8 \, N$ at $60 \, ^\circ C$ by the best fit of Eq. 3.4 to the experimental data. Fig. 3.6 shows that the Weibull distribution represents the experimental data at $60 \, ^\circ C$ with only little deviation.

Failure type 2 is nearly eliminated by the optimized cleaning process with a dehydration step and the careful cleaning of the Si surface before evaporation as described in Appendix A (p. 157). Failure type 1 prevails at higher temperatures. This is due to the difference in the coefficient of thermal expansion of solder ($21.5 \times 10^{-6} \, K^{-1}$) and steel ($16.5 \times 10^{-6} \, K^{-1}$), which causes an additional thermal load on the connection as temperatures increase. The tensile test results indicate that the soldered microfluidic connection is suitable for the proposed operating conditions.
3.2.1 Leak and high pressure test

A Helium leak test measures the permeability of gas through the anodic bonding and the fluidic connection of the microreactor. No leaks are detected above a leak rate value of \(10^{-11} \text{ mbarLs}^{-1}\). We therefore assume that a hermetic seal is formed by anodic bonding between the silicon and glass layer and that the soldered fluidic connection is tight. Long term pressure tests are conducted for over 8 h at an operating pressure of 140 bar and a temperature of 80 °C. No failure of the microreactor is observed during the entire experiment.

3.2.2 Polished cut image

We use a high pressure sample to investigate the soldered connection of a microreactor. A polished cut image is fabricated by wire dicing the sample close to the midplane of the capillary which then is positioned and molded in epoxy. The final polish is done with a diamond slurry of
3.2 Results tensile tests

particles with 0.25 \( \mu m \) diameter (see Appendix A, p. 157).

Figure 3.7: Polished micrograph of the cross section through a soldered fluidic connection to a microreactor.

Fig. 3.7 shows the materials in different shadings. Clearly visible is the microreactor with the etched silicon inlet (600 \( \mu m \) width) and the connected reaction channel (400 \( \mu m \) width). The bonded glass covers the reaction channel. The turned end of the stainless steel capillary is placed on top of the inlet and surrounded by solder. There are several defects seen: A) shows a void, created by the dicing and polishing process. The latter can be concluded by the sharp surface and the rough surface of the void. It is suggested that the void was cut out by the dicing saw. B) shows the separation of the glass and silicon surface. This is introduced by the dicing process as well as the reactor has been tested at high pressure before and showed no failure at this position. C) is more difficult to explain. It either could be a kind of membrane formed during the soldering process. This is not very likely due to the fact that the reactor has been tested for flow and pressure without any problems. Alternatively, C) could represent a similar introduction of solder as on the other sidewall of the capillary inner diameter that has been displaced by the dicing process.

The misalignment of the capillary is about 180 \( \mu m \). Solder fills the capillary but does not block it. The polished micrograph shows clearly that reactant contacting materials are glass, silicon, stainless steel and solder.
3.3 Analytical results

The mechanical strength of a pressurized Si/glass microchannel is estimated by beam theory. The mechanical analysis is divided in three parts according to the different types of failure that can occur in the microchannel. According to this analysis we will be able to set a range for possible materials, channelwidths, channeldepths and process parameters. The failure types in the microchannel are:

- failure due to debonding of the Si/glass interface
- failure of the individual materials due to high mechanical stress
- failure due to thermal stress in the materials
- and/or combinations of the above.

In the following we analyze the above mentioned failure mechanisms and identify the critical loads which can be applied on the microchannel at different channel widths for each case.

Assumptions for beam theory

The calculations were based on the assumptions for basic beam theory

- small deformations (one can calculate the equilibrium of forces on the undeformed beam)
- linear elastic material behavior (Hooke’s law)
- slim beams $h/L \ll 1$ (at least 0.1 to neglect shear stress).

The first two requirements are fulfilled in case of a simplified beam as cover on top of a microchannel. The third requirement is not fulfilled using the geometry $h = 700 \ \mu m$, $L = 200 - 600 \ \mu m$. The ratio of $h/L$ is $O(1)$. At such conditions, we have to take into account shear stress, which occurs in the height direction of the beam. Numerical simulations
could be a possible method to solve the problem of thick beam shear stress. Nevertheless, classical beam theory can be used as the first approximation for the quantification of the different stress contributions in a pressurized microchannel.

### Geometrical basics of the microreactor

The simplified microchannel consists of rectangular channels in Si covered with a glass plate. Channel widths \(w\) are in the range of 100 - 600 \(\mu m\), channel lengths \(L\) in the range of 50 \(mm\) and channel depths \(d\) in the range of 100 - 360 \(\mu m\). The Si wafers are 525 \(\mu m\) \(t_{Si}\) and the Glass wafers 700 \(\mu m\) \(t_{G}\) in thickness, respectively. Fig. 3.8 shows the geometry of the microchannel and its conventions.

**Figure 3.8:** Definition of the channel geometry. (a) Geometry of microchannel. (b) Coordinate system. (c) Deformed channel.

### 3.3.1 Debonding of the Si/glass interface

The theory of minimum energy according to classical mechanics is used to analyze the critical pressure load at which the two materials start to separate. The total energy of the system is

\[
U_{tot} = U_{elastic} + U_{surface} + U_{hydraulic} \tag{3.5}
\]

where
The different parts of the total energy are discussed by (Blom et al., 2001b) and presented in the following sections.

**Elastic energy** $U_{\text{elastic}}$

The elastic energy contains the stored energy in the material by elastic deformation. We consider the glass layer over the microchannel as beam that is rigidly clamped on both sides and loaded with a uniform pressure $p_i$. The deflection $v(x)$ from the centerline is given by (Beitz and Dubbel, 1981)

$$v(x, v_{\text{max}}, c) = \frac{16v_{\text{max}}}{(w + 2c)^4} x^2 ((w + 2c) - x)^2$$ \hspace{1cm} (3.9)

therefore, the elastic energy per unit length is

$$U'_{\text{elastic}} = \int_{0}^{w+2c} \frac{EI_z}{2L} \left( \frac{\partial^2 v}{\partial x^2} \right) \, dx.$$ \hspace{1cm} (3.10)

Inserting 3.9 in 3.10 with the geometrical moment of inertia $I_z$

$$I_z = \frac{L \cdot t^3}{12}$$ \hspace{1cm} (3.11)

results in the analytic term

$$U'_{\text{elastic}}(c, v_{\text{max}}) = \frac{128}{15} \frac{E \cdot t^3}{(w + 2c)^3} v_{\text{max}}^2.$$ \hspace{1cm} (3.12)
Surface energy $U_{surface}$

The surface energy is the energy needed to separate two contacting surfaces. It is defined per unit length by

$$U_{surface}/L = U'_{surface} = 2 \cdot c \cdot \Delta \gamma_b$$  \hspace{1cm} (3.13)

where $\Delta \gamma_b$ is the effective bond energy in $Jm^{-2}$.

Hydraulic energy $U_{hydraulic}$

The hydraulic energy is defined per unit length by

$$U_{hydraulic}/L = U'_{hydraulic} = \int_0^{w+2c} p_i v(x) dx = \frac{8}{15} p_i v_{max} (w + 2c).$$  \hspace{1cm} (3.14)

Total energy $U_{total}$

The total energy per unit length of a pressurized microchannel is

$$U'_{total} = \frac{128}{15} \frac{E \cdot t^3}{(w + 2c)^3} v_{max}^2 + 2 \cdot c \cdot \Delta \gamma_b + \frac{8}{15} p_i v_{max} (w + 2c).$$  \hspace{1cm} (3.15)

The minimum of the total energy of the system defines a stable situation. We now calculate the maximum pressure which can be applied to the microchannel without debonding thus $c = 0$

$$\frac{\partial U'_{total}}{\partial v_{max}} = 0 = \frac{\partial U'_{total}}{\partial c}.$$  \hspace{1cm} (3.16)
This leads to an expression which defines the critical pressure in a microchannel where debonding and therefore the failure of the device occurs

\[ p_{\text{crit}} = \sqrt{24 \cdot Et^3 \Delta \gamma_b \frac{1}{w^2}}. \quad (3.17) \]

The most uncertain value in Eq. 3.17 is the bond energy \( \Delta \gamma_b \). A variety of experimental methods exist to measure the adhesion of bonded wafers (Vallin et al., 2005). The most commonly used is the double cantilever beam method. In this test a metal blade is inserted between the wafer pair and the crack length is measured. The surface energy according to (Maszara et al., 1988) is

\[ \gamma = \frac{3}{8} \frac{Et^3 y^2}{L^4}, \quad (3.18) \]

where \( \gamma \) is the specific surface energy, \( E \) the Young’s modulus, \( t \) the thickness of the wafer, \( 2y \) the thickness of the inserted blade and \( L \) the crack length. A slightly different approach is used by (Go and Cho, 1999) where the blade is inserted prior to anodic bonding. These measurements are conducted with comparable parameters as in our fabrication and the measurement procedure is suitable for anodic bonding. Therefore we choose the lowest bond energy (0.03 \( Jm^{-2} \)) reported in (Go and Cho, 1999) for the calculation.

Inserting the material properties of the used glass and the specific surface energy, a maximum channel width of 515 \( \mu m \) at 150 \( bar \) is derived. Fig. 3.9(a) shows the critical pressure depending on the channel width. Experimental data of burst tests for channel width of 400 – 600 \( \mu m \) shows a maximum pressure applied in the range of 130 \( bar \). The brittle behavior of glass and the not exactly known bond energy explains the deviation from theory. Fig. 3.9(b) shows a photograph of the failed microchannel at 129 \( bar \) with a channel width of 600 \( \mu m \). Therefore, debonding of the glass and Si surface occurred at the channel edge and leads to the failure. The microfluidic connections are not affected. In the case that shear stress has to be accounted for the needed surface energy
of a pressurized channel can be calculated by (Vallin et al., 2005)

\[
2\gamma = \frac{p_i^2 w^4 (1 - \nu^2)}{24Et^3} \left( 1 + \frac{6\alpha_s t^2}{w^2(1 - \nu)} \right), \tag{3.19}
\]

where \(\alpha_s\) is the shear coefficient, usually set to 1.5 for rectangular cross sections.

**Figure 3.9:** Theoretical critical pressure when debonding occurs depending on the channel width. (a) Graph of Eq. 3.17. (b) Photograph of a 600 \(\mu\)m microchannel debonded at 129 bar.

### 3.3.2 Maximum stress in the materials

Basic flexural stress theory is used to estimate the bending stress in glass and Si.

**Flexural stress in glass**

The maximum bending stress in the glass is

\[
\sigma_{b,\text{max}} = \frac{|M_{b,\text{max}}|}{W_y} \tag{3.20}
\]
with

\[ |M_{b,\text{max}}| = \frac{1}{12} p' \cdot w^2 \]  \hspace{1cm} (3.21)

and

\[ W_y = \frac{I_z}{t_{glass}/2} \cdot \]  \hspace{1cm} (3.22)

With the acceptable maximum flexural strength of glass divided by the common safety factor of 1.5 (\(\sigma_f = 25 \text{ MPa/1.5}\)) a critical pressure can be calculated by

\[ p_{\text{crit}} = \frac{\sigma_f \cdot W_y \cdot 12}{w^2 \cdot L}. \]  \hspace{1cm} (3.23)

This result leads to a theoretical pressure of 470 bar that can be applied to a channel width of 500 \(\mu m\) and a channel length of 50 mm.

**Flexural stress in Si**

The same calculations as for glass can be applied, but the moment of inertia \(I_z\) is now dependent on the channel depth \(d\)

\[ I_z = \frac{L \cdot (t_{Si} - d)^3}{12}. \]  \hspace{1cm} (3.24)

Since Si is a strong material with a maximum flexural strength of about 300 MPa the wall thickness at 500 \(\mu m\) channel width has to be \(\approx 100 \mu m\) (at 150 bar, safety factor = 1.5). This means a channel depth of maximum 425 \(\mu m\) is allowed at a Si wafer thickness of 525 \(\mu m\).
3.3 Analytical results

Estimation of shear stress

In a rigidly clamped beam shear stress is calculated as follows.

$$\|M_b\| \sim L\|Q\|,$$  \hspace{1cm} (3.25)

where $\|M_b\|$ is the maximum absolute bending moment, $L$ is the length of the beam and $\|Q\|$ the maximum absolute shear load. The stress follows from

$$\int \int \sigma_x y dS = M_b,$$
$$\int \int \tau_{xy} dS = Q,$$  \hspace{1cm} (3.26)

$$A \cdot h \cdot \|\sigma_x\| \sim \|M_b\|,$$
$$A \cdot \|\tau_{xy}\| \sim \|Q\|,$$  \hspace{1cm} (3.27)

where $A$ is the surface area of the beam cross section and $h$ the height. Hence, the estimation of shear stress for beams can be derived from Eqs. 3.25 and 3.27

$$\|\tau_{xy}\| \sim \frac{h}{L} \|\sigma_x\|.$$  \hspace{1cm} (3.28)

As declared above $h/L$ is very small for slim beams so that shear stress can be neglected compared to flexural stress. In the case that $h/L$ is $O(1)$, both, shear and flexural stress have the same order of magnitude. Therefore, shear stress cannot longer be neglected. The estimation of a stress tensor of first order is

$$\begin{bmatrix}
\sigma_x & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{bmatrix}$$  \hspace{1cm} (3.29)
and has to be replaced by a second order estimation

\[
\begin{bmatrix}
\sigma_x & \tau_{xy} & \tau_{xz} \\
\tau_{yx} & 0 & 0 \\
\tau_{zx} & 0 & 0
\end{bmatrix}.
\]

(3.30)

The following assumptions can made for a simplified shear stress calculation

- a normal stress distribution is given from slim beam theory
- the shear stress is evenly distributed in z-direction.

The first assumption is fulfilled. The second assumption is only correct for narrow beams. This is not the case in our situation, where the width \( b \) compared to the length \( L \) is \( \gg 1 \). This ratio is \( \mathcal{O}(100) \) in our case.

### 3.3.3 Thermal stress

Thermal stress between the Si and the solder, as well as between the capillary and the solder interface, has to be considered. A thermal stress analysis in the different layers is derived from isotropic plain stress theory. (Lau, 1993) describes the linear elastic isotropic behavior of an axisymmetric disc by

\[
\begin{bmatrix}
\sigma_x \\
\sigma_y \\
\tau_{xy}
\end{bmatrix} = \frac{E}{1 - \nu^2} \begin{bmatrix}
1 & \nu & 0 \\
\nu & 1 & 0 \\
0 & 0 & 1 - \nu
\end{bmatrix} \begin{bmatrix}
\epsilon_x \\
\epsilon_y \\
\epsilon_{xy}
\end{bmatrix}
\]

(3.31)

with

\[
\epsilon_x = \epsilon_y = \alpha \Delta T \sigma_x = \sigma_y \sigma_z = 0.
\]

(3.32)

We assume that the dimensions in \( x \) and \( y \) are the same as the multi-layered structure deforms in axisymmetric mode. This is a conservative analysis.
The stress in the according layers introduced by thermal expansion can now be calculated as

\[ \sigma = \Delta \alpha \cdot \Delta T \cdot E \cdot \frac{1}{1 - \nu} \]  

(3.33)

with \( \Delta \alpha \) representing the difference in coefficients of thermal expansion of the materials and \( \Delta T \) the temperature difference, respectively. We must take into account that the Young’s modulus \( E \) of solder decreases from \( E (T = 25 \, ^\circ C) = 48.7 \, GPa \) to \( E (T = 150 \, ^\circ C) = 24.7 \, GPa \) at elevated temperatures. This reduces the stress in the material. But additionally, the maximum tensile stress is reduced. For an increase of \( \Delta T = 75 \, K \), this results in a stress of 74.6 \( MPa \) in the solder. Experiments with the actual microreactor show that the solder is mechanically stable for temperatures up to 100 \( ^\circ C \) at 136 \( bar \). The solder has a maximum tensile stress of 44 \( MPa \) which is in the same range than the calculated value. The thermal stress in the glass and silicon is 1.8 \( MPa \) and 5.2 \( MPa \), respectively for \( \Delta T = 150 \, K \). This is not critical.

### 3.4 Conclusions and summary

Chapter 3 presents the mechanical characterization of the microfluidic connections and the etched microchannel. Tensile tests of the microfluidic connection in the temperature range of 25—80 \( ^\circ C \) show that different failure types occur. A maximal theoretical pressure of 629 \( bar \) is calculated from the minimum observed tensile load in order to be applied on the microfluidic connections. Experiments with pressurized microreactors show a pressure and temperature resistance of 140 \( bar \) at 80 \( ^\circ C \) for more than 8 \( h \) without failure. Later, chemical reactions could be run in the microreactor at 136 \( bar \) and 100 \( ^\circ C \). The conducted experiments show that the combination of high pressure and temperature is the limiting factor for the soldered microfluidic connections. This is due to the differences in CTE of the involved materials which leads to thermal stress. Since only temperatures in the range of 100 \( ^\circ C \) were applied on the microreactor, the presented soldered microfluidic connection are
suitable for conducting high pressure reactions with supercritical carbondioxide.

The analytical mechanical analysis of the microchannel is estimated by classical beam analysis which can be used as design criteria. The maximum applicable pressure is an inverse function of the square of the channel width. In this case, the strength of the bond between the silicon and glass surface is the limiting factor, not the mechanical strength of either silicon or glass. At a pressure of 150 bar, a maximum channel width of 515 µm is calculated analytically without failure of the device.

The results from the mechanical characterization of the device are used for the dimensioning of the microfluidic channels. A maximum channel width of 400 µm and a channel depth of 340 µm is chosen for the high pressure microreactor.
Chapter 4

Fluid Dynamic

Knowledge about the fluid dynamic behavior is crucial to analyze the performance of a continuous flow microreactor. Phenomena like mixing and residence time distribution strongly depend on flow patterns in microchannels, which differ from their macroscale counterparts. Stratified flow for example, does not exist in microchannels due to the dominating surface tension. The first part of this chapter presents an overview over the fluid dynamics and the governing forces in microfluidic channels. The second part shows results from experiments of pressure drop and residence time distribution in empty and packed bed microchannels at single and two-phase flow conditions. A special section is dedicated to the liquid film analysis in segmented gas-liquid flow through rectangular microchannels. This characterization is intended to define optimal flow conditions for the performance of a chemical reaction at a later stage.

4.1 Fluid dynamic in microfluidic channels

4.1.1 Continuum assumption

The continuum model assumes continuous and indefinitely divisible matter. The continuum model is valid for gases when the mean free path $\lambda$
is much smaller than the characteristic length of the flow $L_c$. The mean free path $\lambda$ of a gas molecule modeled as a rigid sphere that depends on pressure $p$ and temperature $T$ is

$$\lambda = \frac{1}{\sqrt{2\pi n \sigma}} = \frac{kT}{\sqrt{2\pi p \sigma^2}}$$  \hspace{1cm} (4.1)$$

where $n$ is the number of molecules per unit volume, $\sigma$ the molecule diameter and $k$ the Boltzmann constant (Bird, 1994). In the continuum model we assume

(1) linear relation between stress and strain
(2) no-slip boundary condition at fluid-solid interface
(3) linear relation between heat flux and temperature
(4) no-jump condition of temperature at the fluid-solid interface.

If the mean free path is not much smaller than the characteristic length, the flow is not near equilibrium and the above mentioned assumptions are no longer valid. Continuum models (i.e. Navier-Stokes equation) should be used in the applicable range if possible. The mathematical handling is easier compared to molecular models, which have to be applied in the non-continuum region.

**Gases**

The Knudsen number $Kn$ defines the ratio between the mean free path and the characteristic length

$$Kn = \frac{\lambda}{L_c}.$$  \hspace{1cm} (4.2)$$

In general, the continuum assumption is valid when $Kn < 0.1$. Empirically different Knudsen regimes have been determined and presented in Fig. 4.1 after (Gad-el Hak, 1999).
Fig. 4.2 shows the effective limits of approximations made for air with an "average air" molecule diameter of $\sigma = 4.15 \times 10^{-10} \text{ m}$. The mean molecular spacing at standard conditions is $\delta_0 = 3.3 \times 10^{-9} \text{ m}$.

Figure 4.2: Limits of different approximations. Adapted from (Bird, 1994).
Liquids

Since the concept of mean free path is not very useful for liquids, there is no accurate information under which conditions the basic assumptions for continuous matter fail. The situation is more complex than in gases and experimental data shows a contrary result. But in general the incompressible Navier-Stokes equations describe the liquid flow in most microfluidic applications. An approximation of the beginning of non-Newtonian fluid behavior is given when the shear rate $\dot{\gamma}$ exceeds twice the molecular frequency scale (Gad-el Hak, 1999)

$$\dot{\gamma} = \frac{\partial u}{\partial y} \geq 2\tau^{-1}$$  \hspace{1cm} (4.3)

with

$$\tau = \left( \frac{m\sigma^2}{\varepsilon} \right)^{1/2},$$  \hspace{1cm} (4.4)

where $\tau$ is the molecular time scale, $m$ the molecular mass, $\sigma$ the molecular diameter and $\varepsilon$ the molecular energy (Lennard-Jones potential). The time scale in Eq. 4.4 is extremely small for common liquids. Water, for example, has a $\tau = 8.31 \times 10^{-13}$ s at standard conditions. This results in very high shear rates at which the continuum approach fails. Therefore, a non-Newtonian behavior of the liquid has to be considered only in extremely small devices at high speed or for polymer with high molecular weight.

(Kleinstreuer, 2003) discusses alternative $Kn$ numbers for liquid and gas-liquid systems, where the mean free path is replaced by the intermolecular length. The continuum approach is valid for $Kn < 0.1$. The Navier-Stokes equation holds in microchannels down to a feature size of 0.1 $\mu$m for water at standard conditions. The global $Kn$ number for liquids is

$$Kn = \frac{\lambda_{IM}}{L_c}$$  \hspace{1cm} (4.5)

where $\lambda_{IM}$ is the intermolecular length of the molecules (for water = 3 $\AA$). The above discussion shows that the continuum approach and the
4.1 Fluid dynamic in microfluidic channels

Navier-Stokes equation describes the fluid flow of the presented microreactor. The Navier-Stokes equation for an incompressible fluid and the corresponding conservation of mass is

\[ \rho \frac{Du}{Dt} = \rho f - \text{grad } p + \eta \Delta u \quad (4.6) \]
\[ \text{div } u = 0 \quad (4.7) \]

with \( u \) the velocity, \( f \) the volumetric forces, \( p \) the pressure, \( \rho \) the density and \( \eta \) the dynamic viscosity of the fluid.

4.1.2 Characteristic dimensionless numbers

Fluid flow in microchannels is particularly defined by high interfacial forces and low Re numbers. The analysis of the scale of forces in microfluidic systems enables the characterization of the flow. Important dimensionless groups are listed in Eqs. 4.8-4.11.

Reynolds number \( Re \)
\[ \frac{uL_c\rho}{\eta} = \frac{\text{inertial force}}{\text{viscous forces}} \quad (4.8) \]

Capillary number \( Ca \)
\[ \frac{\eta u}{\sigma} = \frac{\text{viscous forces}}{\text{interfacial forces}} \quad (4.9) \]

Bond number \( Bo \)
\[ \frac{g\Delta \rho L_c^2}{\sigma} = \frac{\text{gravitational forces}}{\text{interfacial forces}} \quad (4.10) \]

Weber number \( We = Re \cdot Ca \)
\[ \frac{\rho u^2 L_c}{\sigma} = \frac{\text{inertial force}}{\text{interfacial forces}} \quad (4.11) \]

with \( u \) the fluid velocity, \( \rho \) the fluid density, \( \eta \) the dynamic viscosity, \( \sigma \) the surface tension and \( g \) the gravitational constant (9.81 \( ms^{-2} \)). The Reynolds number \( Re \) is typically low in microfluidic systems due to the
small dimensions. In the present microreactor system is $Re < 100$ for gas-liquid-solid reactions and $Re < 500$ for reactions using $scCO_2$ as solvent. This implies a laminar flow regime. The capillary number $Ca$ in the range of $10^{-4} - 10^{-3}$ expresses the dominance of interfacial forces. The Bond number $Bo$ is often used as a criterion for the definition of a capillary. A channel is defined as capillary, as soon as a gas bubble is no more rising in a liquid filled vertical channel. This is formulated by (Bretherton, 1961) as

$$Bo = \frac{g \Delta \rho L_c^2}{\sigma} < 3.368.$$  \hfill (4.12)

Even though there is no term for viscosity or geometrical aspects of the channel included, this criterion can be used as approximation for the microreactor. The multiphase flow in this thesis is characterized by $Bo$ number in the range of $10^{-2}$. If the influence of inertia diminishes ($We \ll 1$) the left hand side of Eq. 4.6 can be neglected. Thus also body forces can normally be neglected. So Eq. 4.6 simplifies to

$$\text{grad } p = \eta \Delta u.$$  \hfill (4.13)

Eq. 4.13 is called Stokes equation and defines creeping flow. In the present case we calculate $We$ in the range of 0.1 indicating Stokes flow.

### 4.2 Two phase flow regimes

Different flow regimes of gas-liquid flow occur in microchannels. Generally, we distinct between bubbly flow, slug flow, annular flow and churn flow. The regions of superficial velocities where the different flow regime occur are schematically shown in Fig. 4.3. The transition lines should not be interpreted as a discrete border between flow regimes. The transition process depends on several factors like the used fluid pair, the channel roughness, the gas-liquid contact geometry and channel geometry which tremendously influences the location of transition from the different regimes. Additionally to transition regimes, further
classifications for the main regimes such as wavy-annular, annular-dry and wavy-annular-dry flow exist. They are not discussed here.

**Figure 4.3:** Schematic flow regime map of gas-liquid flow in microchannels. $j_i$ is the superficial velocity of the gas and the liquid phase, respectively. Adapted from (de Mas et al., 2003).

Bubbly flow is formed at high superficial liquid velocities and low superficial gas velocities. It consists of spherical gas bubbles with a diameter smaller than $d_h$ surrounded by the liquid phase. Slug flow or so called Taylor flow is developed at intermediate superficial velocities, where elongated gas bubbles alternate with liquid slugs. The present study observes and analyzes this flow regime. The gas bubbles length is larger than $d_h$ and the liquid slugs have a length in the range of $d_h$. A recirculating motion in the liquid occurs due to the slippage between the faster traveling gas bubbles and slower liquid slugs. Compared to single phase flow, Taylor flow shows a narrower residence time distribution (Trachsel et al., 2005) and enhanced mixing (Günther et al., 2004). Increasing the gas flow rate leads to the forming of annular flow by minimizing the dissipation energy. The gas passes the channel
at high velocity in a continuous inner core and is surrounded by a liquid film at the channel wall. Churn flow occurs at very high superficial velocities of both the gas and the liquid phase. It is defined by an unsteady gas-liquid interface. Compared to macroscale ducts, surface effects are more pronounced and gravity effects are negligible in microchannels. This hinders stratified flow from occurring. Stratified flow is formed in horizontal channels where the gas phase with the lower density is allocated at the top and the liquid phase at the bottom of the channel.

4.3 Pressure drop

The single phase pressure drop per length in a straight channel is calculated with the following formula (Shah and London, 1978)

\[
\frac{\Delta p}{L} = Re \cdot f \frac{\eta u}{2d_h^2},
\]

(4.14)

where \(\Delta p\) is the pressure loss over a certain length \(L\) of the channel, \(Re\) the Reynolds number, \(f\) a dimensionless friction factor, \(\eta\) the dynamic viscosity, \(u\) the velocity and \(d_h\) the hydraulic diameter of the channel. For the calculation of the pressure drop in an empty rectangular channel the friction factor \(f\) can be calculated by (Shah and London, 1978)

\[
f = \frac{24}{Re} \left(1 - 1.3553\alpha + 1.9467\alpha^2 - 1.7012\alpha^3 + 0.9564\alpha^4 + 0.2537\alpha^5\right),
\]

(4.15)

where \(\alpha\) is the aspect ratio of the channel (\(\alpha \leq 1\)). The Ergun equation (Ergun, 1952) describes the pressure drop in a channel packed with particles

\[
\frac{\Delta p}{L} = f_p \cdot \frac{\rho u_0^2}{d_p} \cdot \frac{1 - \epsilon}{\epsilon^3},
\]

(4.16)
where $\Delta p$ is the pressure drop across the bed, $L$ the length of the bed, $d_p$ the mean particle diameter, $\rho$ the fluid density, $\eta$ the dynamic viscosity of the fluid, $u_0$ the superficial velocity in the empty channel and $\epsilon$ the void fraction of the bed. The friction factor $f_p$ is described by

$$f_p = a \frac{(1 - \epsilon)}{Re_p} + b,$$

(4.17)

where $a$ and $b$ represent the Ergun coefficients for the fraction of viscous and kinetic energy losses of the total pressure drop. These coefficients may vary in different packed beds due to different shape and porosity of the bed. $Re_p$ is the particle Reynolds number based on the particle diameter and the superficial velocity in the empty channel. Eq. 4.17 in Eq. 4.16 leads to

$$\frac{\Delta p}{L} = a \frac{(1 - \epsilon)^2 \eta u_0}{\epsilon^3 d_p^2} + b \frac{1 - \epsilon \rho u_0^2}{\epsilon^3 d_p}.$$  

(4.18)

Eq. 4.18 is used for the determination of the coefficients to characterize the packed bed microreactor. The experimental setup is tested with water to show the influence of the manifolds and tubings between the pressure sensors on the pressure drop. Instead of a microreactor a 10 mm capillary was inserted to simulate the microfluidic connections on the microreactor.

Fig. 4.4 shows that the pressure drop in the setup can be described by theory in good agreement with the experimental results. This finding allows to detect the actual pressure drop in the microreactor.

Fig. 4.5 shows the single phase pressure drop through a packed bed microreactor. The microreactor has a channel width of 1 mm and a channel depth of 340 $\mu$m. Standard catalyst particles are used and a packed bed length of 26 mm is measured. The Ergun equation is applied with the standard coefficients $a = 150$ and $b = 1.75$. The porosity of the bed is $\epsilon = 0.59$ as mean value of measured data. A value of $\epsilon = 0.40 - 0.42$ is common for randomly packed beds (VDI, 2006). The measurement of the porosity in the packed bed microreactor was
Figure 4.4: Pressure drop in the experimental setup at different flow rates measured with water. The error bars represent the variance of the different experiments. The relative error in the flow rate is 0.5%, given by the supplier.

done by measuring the weight and length of the packed bed. A higher value than for randomly packed beds is reasonable in microreactors since local porosity fluctuations in the radial and axial direction have to be considered at small ratios of $d_h/d_p$. Additionally, these effects increase the integrated porosity of the packed bed. All pressure drop experiments are conducted at system pressures of 10 and 20 bar but as expected no change is observed since the fluid is assumed to be incompressible.
4.4 Residence time distribution

4.4.1 Experimental

The residence time distribution (RTD) in the microreactor is measured applying a measurement technique developed in a prior work of this thesis (Trachsel et al., 2005) that used microreactors fabricated from PDMS. A microreactor volume usually is in the range of $\mu L$. Therefore, an "on-chip" pulse generation is favored since standard injection techniques have injection volumes several times larger than the reactor volume itself. Additionally, manifolds and microfluidic connection would distort the measurement and not represent the actual residence time distribution of the microfluidic channel.

Fig. 4.6 shows a scheme of the measurement method. The microreactor is fabricated with a reservoir for tracer liquid which is connected to the main channel. A piezoelectric bending disk is attached on top of the reservoir. By applying a DC voltage the piezo element deflects and
the displaced volume of the reservoir is injected into the main channel as nearly perfect tracer pulse. The elongation of the tracer pulse due to dispersion is monitored using fluorescence microscopy. From the linear relationship of fluorescent intensity and tracer concentration residence time distribution curves can be derived following standard theory (Levenspiel, 1999).

Figure 4.6: Scheme of the measurement technique of residence time distribution in microreactors from (Trachsel et al., 2005).

The microreactor design is adapted for the RTD measurements in order to determine RTD in a packed bed microchannels as used for the heterogeneously catalyzed reaction experiments (see Fig.4.7). The gas and tracer inlets are designed with large pressure resistance in form of small meandering channels. This ensures a stable gas flow and minimal tracer backflow. Ethanol/nitrogen and Rhodamine B are used as fluid pair and as fluorescent tracer, respectively.

An ensemble mean of 5 - 10 experiments of the input and output signals are taken for better statistics. The dimensionless response concentration distributions from a pulse injection (E-curves) are analyzed as follows
4.4 Residence time distribution

**Figure 4.7:** Adapted design of the packed bed microreactor fabricated in PDMS. The field of view (FOV, $1.48 \times 1.12 \text{ mm}^2$) indicates the measurement location of the input and output concentrations with fluorescence microscopy $2 \text{ mm}$ behind the tracer input and the packed bed, respectively. The channel width and depth are $500 \mu\text{m}$ and $140 \mu\text{m}$, respectively. Measurements with two different glass particles sizes are conducted ($x_{50} = 64.5 \mu\text{m}$ and $85.2 \mu\text{m}$). The particles are held in place by micromachined poles at the beginning and the end of the packed bed.

\[
E_k(T_i) = \frac{I_k(t_i)}{\sum_{i=1}^{n} I_k(t_i) \Delta t} \quad (4.19)
\]

\[
\theta = \frac{t_i}{\bar{t}} \quad (4.20)
\]

where $k$ is either the input or output of the flow in the FOV. $I$ is the fluorescence intensity of the Rhodamine B colored fluid, $t$ the time and $n$ the number of recorded images. $\Delta t$ is the time step given by the frame rate of the software, which is between 4 and 8 frames per second (fps) depending on the flow rate. A deconvolution algorithm is performed to obtain the RTD. Eq. 4.21 shows the procedure where $FFT$ and $invFFT$ are the fast Fourier transformation and inverse fast Fourier transformation, respectively. $H(\omega)$ is the transfer function and $F(\omega)$ a Gaussian filter to reduce the noise. $\delta$ is the standard deviation and $BT$ the filter $3 - dB$ bandwidth times the input signal period.
\[ H(\omega) = \frac{\text{FFT(output}(t))}{\text{FFT(input}(t))} \] (4.21)

\[ E(\theta) = \text{invFFT}[F(\omega) \times H(\omega)] \] (4.22)

with

\[ F(\omega) = \frac{1}{\sqrt{2\pi\delta}} e^{-\frac{\omega^2}{2\delta^2}} \] (4.23)

\[ \delta = \frac{\sqrt{\ln(2)}}{2\pi BT} \] (4.24)

### 4.4.2 Experimental results

Fig. 4.8 shows the results for the single phase flow at different liquid flow rates in an empty and packed bed microchannel. The RTD changes from dispersion regime to a pure convection regime with increasing flow rate. In Fig. 4.8(a) both curves are centered at the mean residence time and have a long tail, caused by axial dispersion. The dispersion model (Eq. 4.25) is fitted with a vessel dispersion number of \( VDN = 0.01 \). This can be defined as plug flow. The vessel dispersion number defines the ratio of axial dispersion to the movement of the bulk flow.

\[ E(\theta) = \frac{1}{\sqrt{4\pi(D^*/u_LL)}} \exp\left[-\frac{(1-\theta)^2}{4\theta(D^*/u_LL)}\right] \] (4.25)

vessel dispersion number = VDN = \( \frac{D^*}{u_LL} \) (4.26)

\[ E(\theta) = \begin{cases} 0, & \text{for } \theta < \frac{1}{2}, \\ \frac{1}{2\theta^3}, & \text{for } \theta \geq \frac{1}{2}\end{cases} \] (4.27)

where \( u_L \) is the superficial liquid velocity, \( L \) the length of the microchannel and \( D^* \) the dispersion coefficient. The packed bed has a
slightly broader shape and therefore, dispersion is larger, due to internal recirculation and channeling in the packed bed. The residence time distribution changes to a pure convection regime profile at liquid flow rates of 100 $\mu$Lmin$^{-1}$ (see Fig. 4.8(b) and Eq. 4.27). There is no detectable difference of an empty and packed microchannel with the current setup at this short residence time.

Fig. 4.9 shows the liquid mean residence time for three liquid flow rates at different gas flow rates. The lines indicate the calculated theoretical mean residence time on the basis of the reactor volume and the superficial velocities of both the gas and liquid phase $\bar{t} = \frac{V_R}{(j_G + j_L)}$. The calculated values for the mean liquid residence time at single phase flow ($V_G = 0 \mu$Lmin$^{-1}$) are higher compared to the measured ones. The difference is significant at low flow rates. This can be explained by the little impulse introduced by the tracer injection. The empty channel has a higher mean residence time than the packed bed in the two phase case. This is obvious since the packed bed microreactor has a reduced volume. By increasing the gas flow rate, the mean residence time does not change significantly. This indicates that the liquid flow is not much influenced by the gas flow rate. It also means that the gas bubbles travel faster than their theoretical superficial velocity and that the liquid phase travels slower due to slippage between liquid slugs and gas bubbles.

We fit the experimental curves with the dispersion model and extract the vessel dispersion number in order to analyze two phase flow in the packed bed microreactor. Fig. 4.10(a) shows a comparison of an empty and packed bed microchannel at 20 $\mu$Lmin$^{-1}$ liquid flow rate and 10 $\mu$Lmin$^{-1}$ gas flow rate. The dispersion is higher in the packed bed case and the model fits very well with $VDN = 0.009$ for the empty channel and $VDN = 0.021$ for the packed bed. The comparison with the vessel dispersion number in single phase flow shows that dispersion is reduced in segmented gas-liquid flow in an empty channel. This is due to the separation of the liquid phase by gas bubbles. Although liquid films in the corner and at the wall adjacent liquid slugs can exchange matter in the axial direction. The next section 4.5
Figure 4.8: Measured E-curves of single phase flow in an empty and packed bed microreactor. The packed bed length is 25 mm and $d_h/d_p = 2.4$. The experimental data is fitted with the corresponding models (Levenspiel, 1999). (a) Liquid flow rate $V_L = 20 \mu L/min$. (b) Liquid flow rate $V_L = 100 \mu L/min$. 
Figure 4.9: Measured (markers) and theoretical (lines) mean residence times in an empty and packed bed microreactor at different liquid and gas flow rates.

analyzes these films in more detail. The two phase flow in the packed bed shows higher dispersion than in the empty channel. This indicates that channeling is enhanced in the packed bed and that the liquid flows faster through the packed bed than in the single phase case at the same volumetric flow rate.

Fig. 4.10(b) shows the dispersion coefficients dependent on the capillary number. The dispersion coefficient shows a slight increase of about one order of magnitude for the explored range of data. The empty channel shows lower dispersion as the packed one for the same flow conditions. At higher gas flow rates the dispersion increases in the packed bed and in the empty channel.

The impact of dispersion on chemical reaction is significant. A high dispersion leads to radial concentration gradients in the microchannel. We choose a liquid flow rate of reactant of $23 \mu L min^{-1}$ for the high pressure reaction in order to get a narrow residence time distribution.
Figure 4.10: Effect of the packed bed on two phase gas liquid flow in a microreactor. (a) E-curves. (b) Dispersion coefficient calculated from the best fit of the dispersion model.
4.5 Film analysis

Knowledge about the liquid film thickness in rectangular microchannels is essential, especially for gas-liquid reactions. The flow through a packed bed microreactor is not ideal since the channel to particle diameter ratio $d_h/d_p$ is relatively small ($< 5$) in the case of a microchannel with an acceptable pressure drop. This small ratio leads to a large local porosity at the channel walls where a major part of the fluid passes with little interaction with the catalyst particles. Additionally, an enhanced radial mass transfer to the wall will occur in a thin liquid film. The liquid films in the corner of the microchannel are of great importance to quantify axial mass transfer behavior since the communication of subsequent liquid slugs mainly occurs through the liquid filled corners. The liquid film thickness in segmented gas liquid flow is measured to define this amount of liquid passing at the wall.

4.5.1 Introduction

The average local wall porosity $\epsilon_w$ of a packed bed is (VDI, 2006)

$$\epsilon_w = 1 - 0.513 \left( \frac{d_h}{d_p} \right) - \left( \frac{7}{8} \right) \left( \frac{d_h}{d_p} \right) - \left( \frac{1}{2} \right) \quad \text{for } y/d_p < 1/2 \quad (4.28)$$

where $y$ is the distance from the wall. At $y = 0$ the local porosity is 1 for spherical particles. For a $d_h/d_p = 2.4$ the average local wall porosity is calculated to be 0.59. Fig. 4.11 shows a topographic image of a confocal microscope. The porosity at the wall is calculated with the according microscope software to $0.57 \pm 0.06$. This agrees very well with the theoretical value derived from Eq. 4.28.

(Fairbrother and Stubbs, 1935) investigated the thickness of the remaining liquid film when a long gas bubble ($l_B > 1.5 \, d_h$) passes the capillary. Using a 1 m long circular capillary with an inner diameter of $d_h = 2.25 \, mm$, they found out that the bubble moves faster than the liquid. The velocity of the bubble and the liquid film thickness at the
Figure 4.11: Three dimensional reconstruction of confocal microscopy images at the top wall of a microchannel. The top glass particles ($x_{50} = 65 \, \mu m$) down to a depth of 14 $\mu m$ are seen.

channel wall were found to be dependent on $\sqrt{Ca}$, whereas $Ca$ is the capillary number defined in Eq. 4.9. The film thickness $\delta$ is expressed by

$$\delta = \frac{d_h}{4}\sqrt{Ca}. \quad (4.29)$$

(Marchessault and Mason, 1960) corrected this correlation to

$$\delta = 0.5 \, d_h \sqrt{\frac{\eta}{\sigma}} \left(-0.05 + 0.89\sqrt{u_B}\right). \quad (4.30)$$

(Taylor, 1961) extended the range of experimental data up to $Ca = 2$ where a limiting value of $4 \, \delta / d_h = 0.56$ was suggested. Numerical considerations by (Bretherton, 1961), assuming negligible inertia and gravity effects in horizontal capillaries, refined the results of (Fairbrother and Stubbs, 1935) and led to

$$\delta = 0.66d_h \, Ca^{2/3}. \quad (4.31)$$
(Irandoust and Andersson, 1989) did experimental research on upward and downward Taylor flow in vertical tubes of an inner diameter of \( d_h = 1 - 2 \) \( \text{mm} \) and a length of \( L = 0.4 \) \( \text{m} \). They modified the correlation 4.31 to

\[
\delta = 0.18 \, d_h \left[ 1 - \exp \left( -3.1 C^0.54 \right) \right].
\]  

Experiments by (Aussillous and Quere, 2000) with varying fluids and varying tube radii show the following inertia-dependent correlation

\[
\delta \sim d_h \frac{C^2/3}{1 + C^{2/3} - W e}.
\]  

All correlations above for liquid film thickness discuss semi-infinite bubbles in circular capillaries. Fig. 4.12(a) shows a schematic phase distribution in Taylor flow in capillaries. In circular capillaries a film region of constant film thickness is created (4.12(b)). Correlations for circular capillaries were often used for the wall film thickness in square capillaries. In rectangular microchannel we observe the formation of two different film regions: A corner and a wall film region with dimensions of different magnitude (4.12(c)). The gas bubble is non axisymmetric. A transition region between the corner and wall film is observed where the liquid film reaches a minimum thickness. These contact lines of the gas bubble with the channel wall are discussed by (Wong et al., 1995). An axisymmetric gas bubble is formed for higher \( C a \) numbers as the films increase in thickness (4.12(d)). Short gas bubbles in the order of several channel diameter occur in our observed Taylor flow regime. Measurements of the liquid film in square capillaries were conducted by (Kolb and Cerro, 1991) and (Thulasidas et al., 1995). The numerical simulation by (Hazel and Heil, 2002) for the wall film thickness could not be validated by the results of (Kolb and Cerro, 1991).

(Kreutzer et al., 2005) reviewed Taylor flow in circular and rectangular capillaries. In our study we characterize Taylor flow in rectangular microchannels with a hydraulic diameter of \( d_h = 200 \) \( \mu m \) made of silicon and glass. Confocal Laser Scanning Microscopy (LSM) is used for the optical investigation of Taylor flow at different liquid and gas flow rates. LSM enables a precise spatial measurement of liquid and gas distribution in a single optical slice of the microfluidic channel. Measurements are conducted at low \( C a \) in the range of \( \mathcal{O}(10^{-4}) - \mathcal{O}(10^{-2}) \).
4. Fluid Dynamic

Figure 4.12: Scheme of the liquid film distribution in Taylor flow in microchannels. (a) Schematic phase distribution in Taylor flow. The arrow indicates the flow direction. (b) Section $A - A'$ for circular capillaries. (c) Section $A - A'$ at low $Ca$ ($O(10^{-3})$). (d) Section $A - A'$ at high $Ca$ ($O(10^{-1})$).

At this low $Ca$ surface tension dominates and little impurities may cause large deviation in film and bubble geometry in the microchannel due to Marangoni effects. At the limit $Ca \to 0$ (Wong et al., 1995) finds the film in rectangular microchannels to be non uniform in thickness in lateral and axial direction. We measure the time average film thickness of a passing Taylor flow in a microchannel. Experimental determination of film thickness is crucial since numerical methods have difficulties to resolve the thin films which rearrange over a long axial length scale (Hazel and Heil, 2002; Taha and Cui, 2006).

4.5.2 Experimental

Confocal Laser Scanning Microscopy has risen to an established optical measurement technique in the field of material, biological and medical science within the last years. The main difference between LSM and conventional microscopy is the pixel wise (serial) transformation of the object with a pointscanner in LSM while the object is simultaneously (parallel) transformed in conventional microscopy. The key advantage of LSM is a confocal aperture which enhances the contrast and reduces scattered light from out of focus object slices.
The possibility depth-wise optical slicing of an object makes this measurement technique beneficial for 3D flow visualization in microchannels by fluorescent microscopy. The main advantage of confocal LSM is the high spatial and lateral resolution in the range of sub micrometers. Depth discrimination and stray light suppression are the main features of confocal LSM. Until now, the LSM suffers from its low temporal resolution in the range of 2-3 optical slices per second. Recently, high speed confocal scanner able to acquire 2000 fps have been introduced in confocal microscopy for \(\mu\)PIV measurements (Kinoshita et al., 2007). Confocal microscopy has been used in microfluidic research mainly for the characterization of mixing (Stroock et al., 2002), 2D and 3D velocity measurements by \(\mu\)PIV (Park et al., 2004) and the monitoring of chemical reactions by Raman spectroscopy (Fletcher et al., 2003). Fig. 4.13 shows the experimental setup.

![Figure 4.13: Experimental setup for the confocal LSM measurements of segmented gas-liquid flow.](image)

**Figure 4.13:** Experimental setup for the confocal LSM measurements of segmented gas-liquid flow.
Resolution LSM

It is necessary to define a new optical coordinate "Airy unit" $AU$ in order to represent the resolution independent on the objective.

$$1AU = \frac{1.22 \bar{\lambda}}{NA}$$

(4.34)

where $\bar{\lambda}$ is the wavelength of the illuminating laser light and $NA$ the numerical aperture of the objective. $AU$ is primarily used to normalize the pinhole diameter. Axial and lateral resolution is expressed by two terms; a wave-optical term and a geometric-optical term. The geometric-optical effect on the pinhole can be neglected at small pinhole diameter $PH$. As our measurements are conducted at $PH = 1\, AU$ the pinhole is not considered to be infinitely small. Therefore, the optical slice thickness, axial and lateral resolutions are defined by the following expressions (Pawley, 2006):

Optical slice thickness:

$$\sqrt{\left(\frac{0.88\lambda_{em}}{n - \sqrt{n^2 - NA^2}}\right)^2 + \left(\frac{\sqrt{2n \cdot PH}}{NA}\right)^2}$$

(4.35)

Axial (z) resolution:

$$\frac{0.88\lambda_{exc}}{n - \sqrt{n^2 - NA^2}}$$

(4.36)

Lateral (xy) resolution:

$$\frac{0.51\lambda_{em}}{NA}$$

(4.37)

where $\lambda_{em,exc}$ are the wavelengths of the emitting and exciting light, respectively, $n$ is the refractive index of immersion liquid, $NA$ the numerical aperture of the objective and $PH$ in $\mu m$. The calculated axial and lateral resolution in the presented study are 2.15 $\mu m$ and
0.46 μm, respectively.

The serial operation mode of a LSM leads to a limited temporal resolution of the measurement. Our measurements were conducted with a pixel time of 0.81 μs. Thus, a frame of $1024 \times 1024$ pixel$^2$ is recorded in 0.85 s. A stack of 200 optical slices is accomplished in 170 s.

Stationary Taylor flow in rectangular microfluidic channels is characterized by the alternating flow of gas bubbles and liquid slugs. The subsequent liquid slugs are connected to each other via liquid films at the channel wall and in the corners of the channel. The temporal resolution of the LSM is too low, to obtain a sharp instantaneous 3D image of a channel section. 1024 pictures in the direction of the channel length are averaged over a length of 420 μm to analyze the films in Taylor flow. The regions of permanent liquid films are then indicated by higher intensity than the core region of the channel where gas and liquid passed by during the measurement.

**Image processing**

Fluorescence microscopy is used to visualize the liquid phase distribution in the microfluidic channel. Fluorescein (peak emission = 520 nm) is added to the liquid phase and excited with a laser of 488 nm wavelength. A low pass filter ensures that only the emitted light is detected by the photomultiplier.

The microreactor is placed on precision stage connected via flexible tubing to gas and liquid feed as described in section 4.5.2 during measurement. We used a 20× long working distance objective ($N.A = 0.6$) with correction for different cover glass thicknesses. The correction is necessary for a correct reproduction of the length scales in depth through the glass cover of the microfluidic channel. Optical slices in channel depth are recorded with a confocal laser scanning microscope (LSM 5 Pascal, Zeiss). The frame size is $1024 \times 1024$ pixel$^2$ which corresponds to a field of view of $420 \times 420$ μm$^2$. The optical slice thickness is 0.41 μm. Since only the films at the top of the microfluidic channel are observed, the stack size in z-direction is 75 – 100 μm. The pinhole diameter on the microscope is set to a constant value of 112 μm which is equal to 1 AU.
The acquisition time for one pixel is 0.81 $\mu$s and two measurements are averaged per pixel for better statistics.

**Figure 4.14:** Scheme of data analysis for the determination of the film thickness. (a) Optical slices in direction of the channel depth recorded with the LSM. (b) Reconstruction of yz slices. (c) Average image of all yz slices in channel length direction. (d) Average image of the channel cross section with a schematic outline of the channel wall and observed films. Film thicknesses at the channel top ($\delta_f$) and in the corner ($\delta_c$) and the width $w$ are measured.

Fig. 4.14 shows the schematic operations of the data analysis. The acquired images are time averaged pictures of subsequently passing liquid slugs and gas bubbles. By averaging the images in flow direction, regions of permanent liquid coverage have a significant increased intensity compared to regions where both gas and liquid pass through during the acquisition time of a stack of pictures. Edges of the liquid regions and thresholds are detected by the means of the software Matlab. The optical slices are acquired and stored as a stack of pictures (Fig. 4.14(a)). When a xy-frame is recorded, 55% or more of the frame is covered by gas, and thus has zero intensity. The stack is then
sliced in x-direction where each frame represents a slice in direction of the channel length (Fig. 4.14(b)). By averaging all 1024 yz-frames, a distinction between permanently wetted areas and areas of passing liquid and gas can be made via thresholding (Fig. 4.14(c)). The wall film at the channel top ($\delta_f$) and in the film in the two corners ($\delta_c$) are determined by a Matlab code (Fig. 4.14(d)). The robustness of the method was verified by threshold variation.

The channel top wall, the schematic bubble shape and the film width are indicated by the white lines. The channel walls are indicated clearly by applying an automated threshold at the channel edges. Light scattering on the transition from the glass to the thin liquid film and from the liquid film to the gas phase is taken into account for the identification of the film thickness. The wall film thickness is defined by the length from the channel edge to the first minimum intensity. This region showed the highest intensity values and therefore the other parts of the wall film are assigned to light scattering. The corner film thickness is calculated by the diagonal distance between the channel corner and the transition from liquid to the gas phase.

The wall film width is analyzed from the intensity profile at the top channel wall and is indicated by the white lines in Fig. 4.14(d). Higher intensities represent liquid present at the wall. The two minima of the intensity distribution indicate the transition from the corner film to the wall film at the top channel wall. The distance between these points is defined as the film width $w$.

### 4.5.3 Film thickness

The data from confocal microscopy is used to analyze quantitatively film thickness and film width.

Fig. 4.15 shows the plotted results of film thicknesses together with correlations from literature. First, we consider the situation at the corner. The correlation according to (Kreutzer et al., 2005) slightly overpredicts the film thickness of the experimental data. This correlation was used for $Ca$ values ranging from $2 \cdot 10^{-4}$ to 10. The asymptotic value for $Ca \to 0$ by (Wong et al., 1995) is 0.1098. The general decreasing
tendency with decreasing $Ca$ is the same for the measured values and the model. The difference is more pronounced at low $Ca$, where shorter bubbles in the segmented gas liquid flow occur. At higher $Ca$ the gas bubbles elongate and the measurements are better comparable to literature, where mostly semi infinite gas bubbles at higher $Ca$ are found. The corner film thickness is nearly independent from the $Ca$ for small $Ca$ ($Ca < 0.001$). The ratio of the film thickness in the corner to the hydraulic channel diameter remains constant at about 0.1.

![Figure 4.15](image_url)

**Figure 4.15:** Measured film thicknesses for different fluids. Filled symbols represent the film thickness in the corner and open symbols the wall film thickness, respectively.

For the film thickness at the wall, the model by (Bretherton, 1961) (Eq. 4.31) proposes a dependency of $Ca^{2/3}$ also for small $Ca$. The measurements of (Kolb and Cerro, 1991) for a semifinite gas bubble lead to the assumption that no significant change of the film thickness for further reducing $Ca$ occurs at $Ca < 0.01$. Using a smaller channel, our
measurements confirm this trend. For $Ca < 0.01$, the ratio of the film thickness at the wall to the hydraulic channel diameter is constant at a value around 0.02. The uncertainty of the measurements in this range is relatively high due to the limited optical resolution. The measured film thickness is about $\delta_f = 4 \ \mu m$, and the resolution in the $z$-direction is $\pm 2.15 \ \mu m$. The model of (Fairbrother and Stubbs, 1935) (Eq. 4.29) — which is in line with experimental results for $Ca > 0.1$ — can not be adapted to the measurements at $Ca < 0.01$. Therefore, none of the existing correlations describes the experimental data at low $Ca$.

Other authors describe a significant deviation of experimental results of wall film thickness compared to Bretherton’s theory. Thicknesses larger than theory were measured at very low $Ca$. The larger values were contributed either to the surface roughness (Chen, 1986) or to small amounts of adsorbed surface-active contaminants on the gas-liquid interface (Ratulowski and Chang, 1990). The interface becomes more rigid in regions of high surfactant concentrations (bubble front). At low surfactant concentration (film) the surface tension is larger and induces more liquid to flow into the film. This leads to an increased wall film thickness. The latter theory has been developed for long gas bubbles ($l_B > 20 \ d_h$), it is therefore difficult to adapt the results to Taylor flow with bubble length in the order of a few channel diameters. Fig. 4.15 shows the correction of Bretherton’s theory for Marangoni effects (Ratulowski and Chang, 1990). Additionally, the theory by Bretherton is applicable for circular capillaries. In our case of a square microchannel, the wall film thickness is developing on a flat area. In case of low $Ca$, the situation is reduced to a static wetting problem assuming zero velocity in the film. The film thickness then is defined only by the surface tension of the fluid and the wall material. As inertial effects are negligible, a constant film thickness is obtained. This corresponds to the theory of the corner wall thickness, where an asymptotic value for the thickness at $Ca \rightarrow 0$ is obtained (Wong et al., 1995).

### 4.5.4 Film width

Fig. 4.16 shows that the film width is decreasing with increasing $Ca$. This corresponds to the slightly increasing corner film thickness. The
gas bubble becomes more symmetric with increasing corner liquid volume. At the same time the film width decreases (compare 4.12). Former studies report an axial symmetric gas bubble (body) at higher values of $Ca \approx 0.1$ (Kolb and Cerro, 1991). Since the measurements were carried out at lower $Ca$ numbers, this transition is not observed.

### 4.5.5 Film area

The total film area in a channel cross section was calculated assuming a tangential transition from the corner film to the wall and a rectangular shape of the wall film which is calculated with the measured thickness and width. The corner film area is $A_c = 4 \ r_c^2(1 - \pi/4)$. $r_c$ defines the radius of the gas bubble in the corner, that is calculated using geometrical constraints reported in (Kolb and Cerro, 1991). The wall film area is $A_f = 4 \ \delta_f \ w$. The relationship between film area, the bubble velocity ($u_B$), and the liquid slug velocity ($u_S$) can be investigated from the
over all mass balance between a cross section where gas and liquid are present and a cross section through the liquid slug. At steady state and incompressible conditions, assuming zero velocity in the liquid film for horizontal flow, the mass balance leads to the relation

\[ A_B u_B = A_{\text{Channel}} u_S \]  

(4.38)

where \( A_B \) is the area occupied by the gas bubble and \( A_{\text{Channel}} \) the cross section of the channel. This leads to

\[ 1 + \frac{A_c + A_f}{A_{\text{Channel}}} = \frac{u_B}{u_S}. \]  

(4.39)

Eq. 4.39 shows that the bubble velocity is always faster than the liquid slug velocity since the corners of the microchannel are always wetted by liquid and therefore the total film area \( (A_f + A_c) \) does not vanish. The film area is difficult to obtain since the transition area from the wall film to the corner film is hard to resolve. An approximation of the area leads to a ratio of \( (A_f + A_c)/A_{\text{Channel}} \) of about 10% for a water/nitrogen mixture at \( Ca = 0.003 \). The corners account for about 70% of the total film area at the measured \( Ca \) number. Theoretical limits for the liquid covered area are known from literature (Kreutzer et al., 2005). At \( Ca \to \infty \) the total film area covers 61.5% of the channel area. Assuming only corner films at \( Ca \to 0 \) and a maximal bubble diameter in the diagonal direction of 1.2, the minimal total film area is 5.7%.

### 4.6 Conclusions and summary

Flow in microfluidic channels is described by the Navier-Stokes equation since the continuum assumption holds. A look on the governing forces in microfluidics shows that microflow is governed by high interfacial forces and the disappearance of the influence of inertial and gravitational forces. Pressure drop measurements show that standard calculation methods for rectangular ducts and the Ergun equation for packed beds describe the
pressure drop in the microreactor. Residence time distribution is measured in the packed bed microreactor at different flow conditions. The mean liquid residence time is not changed significantly when introducing a gas phase into the liquid flow. This indicates the slippage between the gas and liquid phase in segmented gas liquid flow and indirectly shows the faster velocity of the gas bubble compared to the liquid slug. We see that the packed bed does not significantly enhance dispersion in the single phase case. In two phase flow, channeling is enhanced in the packed bed and increases the vessel dispersion number $D^*/(u_L L)$ from 0.009 to 0.021 for $V_G = 20 \mu Lmin^{-1}$ and $V_L = 10 \mu Lmin^{-1}$. The enhanced dispersion is attributed to a strong channeling of the liquid phase in the packed bed where the dispersion is also enhanced. The dominating surface tension effects enhance the channeling of the liquid and gas phase in the packed bed. The results are used to set the operating conditions of the high pressure reaction in the packed bed microreactor. The liquid flow rate is set to $V^* = 23 \mu Lmin^{-1}$ and the gas flow rate is set as low as possible to achieve a stoichiometric ratio of the reactants and to reduce the dispersion. The accuracy of the experimental setup limits a further lowering of the flow rate. The error is in the range of 0.5 $\mu Lmin^{-1}$ for the liquid feed at the chosen flow rates. The relative error increases at lower flow rates.

Using confocal LSM enables the measurement of average liquid film thickness in transient segmented gas liquid flows. The areas permanently wetted with liquid in the corner and at the top channel wall are investigated. The experimental results show that the film thickness stays nearly constant for small $Ca$ and that it does not vary with different $Ca$. The corner film thickness is in the range of $\delta_c/d_h = 0.09$ and the wall film thickness in the range of $\delta_f/d_h = 0.02$. The wetted areas at the wall cover the channel in the range of 10% whereas the liquid filled corners contribute with about 70% to the total film area. The catalyst packed bed has a higher local porosity at the channel wall due to the small ratio of $d_h/d_p$. Therefore, about 10% of the liquid passes the bed nearly unaffected by the catalyst in the observed gas-liquid segmented flow due to the liquid films at the channel wall.
Chapter 5

High Pressure Reactions

The reaction performance of the fabricated high pressure microreactor is analyzed by means of a model reaction. In this chapter, we use the case of a heterogeneously catalyzed hydrogenation to focus on the feasibility of microreaction technology in high pressure and high temperature chemical reaction engineering. The hydrogenation of cyclohexene is conducted in a packed bed microreactor as a model reaction. The influence of pressure and temperature on the reaction rate is investigated. Optical access into the reaction chamber allows the observation of crucial parameters such as flow patterns, catalyst packing and mixing of the reactants. The three phase gas-liquid-solid reaction is conducted and analyzed in a T-shaped microreactor at pressures up to 50 bar and temperatures up to 70 °C in a first step. $scCO_2$ is used as reaction solvent to further increase the reaction performance. The reaction is conducted as SCF-solid phase reaction in the microreactor. The liquid velocity and phase behavior of the reaction mixture is measured in situ. A mass transfer analysis and the comparison with available performance data of other reactor systems concludes this chapter.
5.1 Introduction

Recently, a number of studies of catalytic hydrogenation (Wiessmeier and Hönicke, 1996; Hessel et al., 2003; Yeong et al., 2004; Kobayashi et al., 2004) have been conducted in different types of microreactors (Kolb and Hessel, 2004; Hessel et al., 2005; Kiwi-Minsker and Renken, 2005). The hydrogenation of cyclohexene at ambient pressure in porous and packed bed microreactors over Pt catalyst is studied by (Losey et al., 2001, 2002). The reaction was mass transfer limited. At temperatures up to 200 °C and ambient pressure, (Surangalikar et al., 2003; Besser et al., 2003) conducted the same reaction in the gas phase over sputtered Pt catalyst where the reaction was limited by the intrinsic reaction rate. Continuous high pressure hydrogenation reactions in small tube reactors with inner diameters of 1 mm and 4 mm have been presented by (Desai and Kappe, 2005; Yoswathananont et al., 2005).

5.2 Experimental

5.2.1 Model reaction

To present the influence of pressure and temperature on the reaction performance in a packed bed microreactor, we investigated the hydrogenation of cyclohexene using commercially available catalyst. The catalyst is Pd on alumina (Al₂O₃) particles (Johnson Matthey, 2 wt% Pd, Typ 31, Product code: 113031) with a catalyst porosity of 0.72. The metal surface to mass ratio is 1.75 m²g⁻¹ and the dispersion is 19.7 % measured with pulsed CO chemisorption (Autochem 2910, Micromeritics, Mönchengladbach, Germany). The BET surface is 157.7 ± 1.3 m²g⁻¹ (Tristar3000, Micromeritics). The reaction formula is given in Fig. 5.1. Hydrogenations are often mass transfer limited where the rate-limiting step is the transport of hydrogen to the active sites of the catalyst. We choose this model reaction for several reasons:

(1) the exothermic character (ΔHᵣ = −118 kJmol⁻¹) offers a possibility to show the advantages of microreactors in temperature
control,

(2) a change in the operating variables \((p, T)\) has significant influence on the reaction rate

(3) this reaction serves as a model for many significant reaction classes in the chemical, process and petroleum industries

(4) it is well described in the literature (Madon et al., 1978; Segal et al., 1978; Gonzo and Boudart, 1978; Watson and Harold, 1993).

\[
\begin{align*}
\text{C}_6\text{H}_{10} + \text{H}_2 &\rightarrow \text{C}_6\text{H}_{12} \quad \text{(5.1)} \\
\text{C}_6\text{H}_{10} &\rightarrow \text{C}_6\text{H}_6 + \text{H}_2 \quad \text{(5.2)}
\end{align*}
\]

**Figure 5.1:** Reaction formula of the catalytic hydrogenation of cyclohexene to cyclohexane.

The hydrogenation (Eq. 5.1) is favored at low temperatures and the formation of benzene by dehydrogenation (Eq. 5.2) is favored at high temperatures and low partial pressures of \(H_2\). No benzene was detected in our temperature range during all experiments.

The equilibrium constant of the reaction equation 5.1 is in the order of \(1 \times 10^{15}\) at \(T = 273.15 \, K\). This leads to the assumption of an irreversible reaction.

The reaction rate is reported to be first order with respect to hydrogen and zero-order with respect to cyclohexene (Madon et al., 1978). The reaction rate is described by

\[
r = k c^l_{H_2} \quad \text{(5.3)}
\]

where \(k\) is the reaction rate constant and \(c^l_{H_2}\) is the concentration of dissolved hydrogen in liquid cyclohexene depending on pressure and
temperature. The concentration of dissolved hydrogen in cyclohexene is calculated by Henry’s law and varies linearly with pressure in the temperature range of 30 − 100 °C and in the pressure range of 10 − 100 bar from 0.0025 − 0.035 molH2/molC6H10 (Herskowitz et al., 1983).

The activation energy in case of a Pt catalyzed reaction is 26.03 kJmol$^{-1}$ (Madon et al., 1978). The effect of pressure on the reaction kinetics according to the transition-state theory are of minor importance. A rate increase or decrease depending on the negative of positive activated volume (typical values are -30 – 30 cm$^3$mol$^{-1}$) in the range of 3.5 is reported for high pressure reaction in solution, increasing the pressure from atmospheric to 1000 bar (Baiker, 1999). As our experiments are conducted in a much lower pressure range, these effects are neglected for the calculations.

### 5.2.2 Materials

Hydrogen and CO$_2$ (Pangas) are used as supplied with a purity of 99.999% and 99.995%, respectively. Cyclohexene (purity > 99%) was purified by distilling at 80 °C and adding iron chloride. During the preparation of the cyclohexene any possible contact with air is avoided. The peroxides content is reduced by distilling from 2 mgH$_2$O$_2$L$^{-1}$ to a not detectable amount using a colorimetric peroxide test (Merckoquant, Merck). The catalyst is exchanged for every experiment when using scCO$_2$ to ensure proper catalyst activity. The catalyst weight in the range of 0.5 − 1 mg is determined by measuring the weight of the dried empty and filled microreactor. Also, the catalyst weight is measured before entirely inserting it into the microreactor. This method leads to the same results. For each experiment, the catalyst is activated for 90 min at 70 °C with a hydrogen flow of 5 mLmin$^{-1}$ at 20 bar. A typical experiment lasts about 100 min.
5.2.3 Analysis

Samples are collected in a sample vial after the back pressure regulator. The vial is cooled in an ice water bath and the product is diluted in toluene to dissolve the product for GC analysis. The conversion is analyzed offline by GC-MS. The three highest conversion values at steady state conditions are averaged to calculate the maximum reaction rates. No side products are detected by GC-MS and the cyclohexene conversion $X_{C_6H_{10}}$ is calculated from the chromatograms, where linearity between peak area and concentration is checked in the range of used conditions. The conversion rate $r$ per catalyst mass is therefore:

$$r = \frac{X_{C_6H_{10}} \cdot V_{C_6H_{10}} \cdot \rho_{C_6H_{10}}}{m_{cat} \cdot M_{C_6H_{10}}}.$$  \hspace{1cm} (5.4)

$V_{C_6H_{10}}$ is the volumetric flow rate, $\rho_{C_6H_{10}}$ the density and $M_{C_6H_{10}}$ the molar mass of cyclohexene, respectively. As the feed is at constant temperature, the density is constant for all experiments. $m_{cat}$ is the catalyst mass.

5.3 Experimental setup

5.3.1 Microfluidic channel design

T-shaped design

The continuous solid catalyzed three phase hydrogenation experiments are conducted in the T-shaped microreactor. The reaction takes place in a straight 36 mm long single reaction channel 340 $\mu$m in depth and 400 $\mu$m in width filled with catalyst particles. The hydraulic diameter $d_h$ is 370 $\mu$m. Inlet and outlet holes are 600 $\mu$m in diameter. The gas and liquid streams are fed via two side channels and contacted in a static mixer consisting of etched columns with a diameter of 100 $\mu$m and a distance of 100 $\mu$m in between them. The static mixer induces the mixing of the gas and the liquid phase. A 10 mm long mixing section
enabled the gas phase to completely saturate the liquid before entering the packed bed. Fig. 5.2 shows a photograph of the device with a channel width of 1 mm. The catalyst particles are placed in the microreactor via a side channel by applying a vacuum at the outlet. Filter elements near the common outlet (length = 300 µm, width = 50 µm with 50 µm space in between) keep the catalyst particles within the microreactor. Ultrasonic treatment was used to generate a randomly particle distribution in the microchannel. A packed bed structure extends to a length of about 25 mm in the microchannel.

\[ \text{scCO}_2 \text{ design} \]

The final high pressure microreactor design suitable for a reaction at maximum 136 bar and 100 °C is shown in Fig. 5.3. 5.3(a) shows a photograph of the channel design through the glass and Fig. 5.3(b) represents the schematic of the different sections of the microreactor. The mixing and the reaction of the used fluids is realized on chip in order to make use of the advantages of microfabrication and to follow the concept of an integrated microreactor manifold. The single channel continuous flow microreactor consists of an inlet, a mixing and reaction section. The narrow inlets from the side into a main stream are designed to generate a stable segmented gas-liquid flow of substrate and hydrogen. This is then dissolved by a side inflow of carbondioxide. The 64.6 mm long mixing section allows the reactants to mix and generates a single phase reaction mixture with scCO\(_2\). Compared to the T-shaped design, a longer mixing section is necessary since the addition of CO\(_2\) leads to higher superficial velocities in the channel. The meandering shape of the channel enhances mass transfer in the radial direction when hydrogen bubbles are present (Günther et al., 2004). The catalyst particles are inserted via a side channel into the microreactor forming a packed bed of a maximum length of 26.5 mm. Micromachined sieves at the entrance and exit of the packed bed define the length of the packed bed. We choose a maximum channel width of 400 µm, adapted from the mechanical strength of the Si/glass microreactor (see chapter 3). The inlets and outlets have a circular shape and a diameter of 400 µm on the front side and 600 µm on the backside allowing a better positioning of the capillary.
Figure 5.2: Photograph of a T-shape microreactor design and according micrographs of the entrance (A) and exit (B) of the packed bed.
Figure 5.3: Microreactor design. (a) Photograph of the Si/glass microreactor. (b) Schematic of the channel design.
5.3.2 Experimental setup

A versatile high pressure experimental setup for continuous operation as shown in Figs. 5.4 and 5.5 is used for the experiments. The setup allows the individual adjustment of the liquid and the gas flow rates as well as the system pressure up to 170 bar. Limiting factors are the stainless steel on/off valves for 1/16”o.d. tubing. Stainless steel and polyetheretherketone (PEEK) capillaries (o.d. = 1.56 mm, i.d. = 0.5 mm) are used as tubing. High pressure PEEK connections (Upchurch Scientific) provide a leak tight connection of the microreactor to the setup. CO$_2$ and C$_6$H$_{10}$ are fed as liquid phase by two water cooled high pressure syringe pumps (ISCO, 260D) with an accuracy of ±0.5% and 0.5 μLmin$^{-1}$ maximum seal leakage. A high pressure mass flow controller (F-230M, Bronkhorst) with an accuracy of ±0.3% controls the hydrogen flow. An automated needle valve back pressure regulator (BP-1580-81, Jasco), accuracy ±2 bar, controls the pressure in the microreactor. Data of pressure (Endress and Hauser, accuracy ±1 bar) and temperature (Thermocouple K-type, Thermocoax) is acquired online via LabView software. The microreactor is placed in an oil bath for reactions at elevated temperatures. The pressure drop across the packed bed is measured in all three phase experiments and is between 0.4 – 0.5 bar. In the case of a single phase reaction using scCO$_2$ as reaction solvent the measured pressure drop is < 1 bar.

5.4 Results of the three phase reaction

5.4.1 Flow regime and residence time

The flow patterns in the microreactor as depicted in Fig. 5.6(a) are observed at ambient temperature and pressures ranging from 5 to 50 bar by laser induced fluorescence (LIF) using Rhodamine B as fluorochrome. Fig. 5.6(b) shows a schematic of the flow pattern in the microreactor. The fluid pair methanol/nitrogen is applied for the flow characterization instead of cyclohexene/hydrogen because of the immiscibility of the Rhodamine B solution in cyclohexene. The capillary numbers for
Figure 5.4: Scheme of experimental setup. (1,2) Cooled high pressure syringe pumps. (3) Hydrogen mass flow controller. (4) Packed bed microreactor. (5) Back pressure regulator. (6) Sample vial.

Figure 5.5: Photograph of the experimental setup. The enlarged view shows the feed lines for the reactants.
the reaction mixture and substituted system were \( Ca = 0.0037 \) and \( Ca = 0.0038 \), respectively. The Reynolds numbers were \( Re = 73 \) for cyclohexene/hydrogen and \( Re = 81 \) for methanol/nitrogen. The close values of the different Ca and Re numbers result in the same flow regime for both systems. Fig. 5.6(c) shows a typical LIF micrograph of a liquid slug.

Figure 5.6: Microreactor design. (a) Photograph of the Si/Glass microreactor. An alumina plate is attached to the capillaries for better handling of the reactor. High pressure fittings (Upchurch Scientific) are used for the connection with the experimental setup. (b) Schematic of the packed bed microreactor during operation. The catalyst inlet/outlet is closed during operation. (c) Fluorescent micrograph of a liquid slug in an empty microchannel 10 \( \text{mm} \) from the mixing section. The system pressure is 20 \( \text{bar} \), \( V_L = 20 \mu \text{Lmin}^{-1}, \) \( V_G = 20 \text{mLmin}^{-1} \). The measured length of the liquid slug is indicated. The channel width is 400 \( \mu \text{m} \).

A set of LIF experiments in an empty microchannel are conducted at pressures up to 50 \( \text{bar} \) in order to identify the flow regime and the liquid slug velocities in the microchannel. Superficial velocities are kept constant at \( j_L = V_L / A = 0.0025 \text{ ms}^{-1} \) and \( j_G = V_G / A = 0.1225 \text{ ms}^{-1} \), where \( A \) is the cross sectional area of the channel. The flow regime is identified as segmented gas-liquid flow with long gas bubbles extending the field of view of the LIF measurement setup (740 \( \times \) 560 \( \mu \text{m}^2 \)). In a set of 200 images recorded with a frame rate of 5 Hz, the liquid
slug frequency is 0.1 – 0.4 Hz. Liquid slug lengths are in the range of 193 – 319 µm. This indicates that part of the fluid is flowing through the microchannel as a wall flow. Double frame images with a time difference of 100 µs are taken from liquid slugs to calculate its velocity. The average liquid slug velocity measured is 0.15 ± 0.05 ms⁻¹. When increasing the system pressure, no significant change of the liquid slug length, liquid slug velocity or frequency is observed. Assuming the same velocity for both the liquid and the gas phase in the microchannel, an average superficial velocity of 0.13 m s⁻¹ for both phases is calculated. The actual liquid slug velocity is lower in the range below 5% (see chapter 4.5.5). But the calculated value is in the same range than the experimental results.

The measured liquid slug velocity is used to calculate the mean liquid residence time. The latter is 0.17 s for an empty microchannel and 0.07 s for a randomly packed bed (porosity = 0.4) of 26 mm in length. Since the actual liquid flow through the packed bed is not known as by-passing, axial dispersion and stagnant regions occur. The liquid residence time can only be estimated to be in the range of the above calculated values.

**5.4.2 Reaction performance**

The hydrogenation of cyclohexene is conducted at constant superficial velocities of both the gas and the liquid phase. The liquid flow rate is kept constant at 20 µLmin⁻¹ as the liquid phase is assumed to be incompressible. The mass flow rate is varied with pressure and temperature from 5 mLmin⁻¹ (p = 5 bar, T = 23 °C) to 50 mLmin⁻¹ (p = 50 bar, T = 23 °C) to provide a constant volumetric gas flow rate. The gas mass flow rate is adjusted for higher pressures and temperatures assuming ideal gas conditions. This correction in the gas flow rate changed the stoichiometric factor for the total system from 1.1 (V_L = 20 µLmin⁻¹ and V_G = 5 mLmin⁻¹ at p = 5 bar, T = 23 °C) to 11.3 (V_L = 20 µLmin⁻¹ and V_G = 50 mLmin⁻¹, p = 50 bar, T = 23 °C), where V_i is the volumetric flow rate of the liquid and the gas, respectively. Even though the reaction is exothermic, no cooling of the microreactor is necessary.

A lumped heat transfer coefficient from the microreactor to the envi-
5.4 Results of the three phase reaction

The environment is $24 \, Wm^{-2}K^{-1}$ (see Appendix B, p. 165). Therefore, the heat loss of the microreactor device dominates the heat generation of the reaction above a minimum temperature difference of $4.6 \, K$ for a conversion of 0.4.

The same catalyst activity is maintained for several experiments. Deactivation is prevented by an in-line peroxide trap containing alumina (Arunajatesan et al., 2001). No change in catalyst activity is observed due to the short total experiment duration.

The influence of pressure and temperature on the reaction rate is investigated where the reaction rate $r$ is defined as the moles of product formed per unit mass of catalyst per unit time. Fig. 5.7 shows the reaction rate as a function of the system pressure measured at the reactor outlet. At higher pressure there is an increase of the reaction rate due to an increase of the hydrogen solubility in cyclohexene.

![Graph: Observed reaction rate for the hydrogenation of cyclohexene for pressures from 1 – 51 bar at ambient temperature. $V_L = 20 \, \mu Lmin^{-1}$, $V_G = 1 – 50 \, mLmin^{-1}$. The reaction is conducted below stoichiometric conditions at a pressure of 1 bar.]

**Figure 5.7:** Observed reaction rate for the hydrogenation of cyclohexene for pressures from 1 – 51 bar at ambient temperature. $V_L = 20 \, \mu Lmin^{-1}$, $V_G = 1 – 50 \, mLmin^{-1}$. The reaction is conducted below stoichiometric conditions at a pressure of 1 bar.

Fig. 5.8 shows the temperature dependence of the reaction rate. The conversions of the measured data ranged from 2.1 – 6.8% at 6 bar and 15 – 35.2% at 51 bar. An activation energy of $E_A = 10.7 \, kJmol^{-1}$ is calculated using the Arrhenius equation and the slope in Fig. 5.8(a).
Such small activation energies derived from the observed reaction rate and compared to literature values (Madon et al., 1978) indicate a mass transfer limited reaction. Fig. 5.8(b) shows the reaction rate as a function of temperature at two different pressures. The reaction rate increases with temperature for two reasons. First, the rate constant increases with temperature in the exponential term of the Arrhenius law. Second, the solubility of hydrogen in the organic solvent increases with temperature, as it does with pressure. The deviations in reaction rate at the same reaction conditions can be explained by different flow paths through the packed bed and therefore a change in the mass transfer behavior.

5.4.3 Mass transfer analysis

The diffusion coefficient of hydrogen in cyclohexane as a function of temperature after (Snijder et al., 1994) is

\[
D_{H_2\infty} = 4.78 \times 10^{-4} e^{-3239 K/T} \ [m^2 s^{-1}]. \tag{5.5}
\]

Batch experiments at \(p = 50 \text{ bar}\) are conducted. An activation energy of \(E_A = 16.8 \text{ kJmol}^{-1}\) and a reaction rate constant \(k_{surf} = 2.98 \times 10^{-3} \text{ cm}^{-1} \text{s}^{-1}\) is calculated. This corresponds to a volumetric reaction rate constant of \(k_{vol} = 15.5 \text{ s}^{-1}\).

An effectiveness factor of \(\eta = 0.4 \ (T = 50 \ ^\circ C)\) and \(0.8 \ (T = 75 \ ^\circ C)\) is calculated iteratively using the definition of the Thiele modulus \(\Phi\) (Eq. 5.6) and the effectiveness factor \(\eta\) (Eq. 5.7) for a first order reaction

\[
\Phi = \frac{r_p}{3} \sqrt{\frac{r_{obs} \rho_{app}}{\eta c_{as} D_{eff}}}, \tag{5.6}
\]

\[
\eta = \frac{1}{3 \Phi} \left( \frac{1}{\tanh(3\Phi)} - \frac{1}{3\Phi} \right), \tag{5.7}
\]

where \(r_p\) is the particle radius, \(r_{obs}\) the observed reaction rate, \(\rho_{app}\) the apparent particle density, \(c_{as}\) the hydrogen concentration at the catalyst.
Figure 5.8: (a) Arrhenius plot for the model reaction at $p = 5\text{ bar}$ and $p = 50\text{ bar}$. Temperature varies from $23\ ^\circ\text{C}$ to $75\ ^\circ\text{C}$. The observed reaction order to hydrogen is 0.68. The linear regression equation is: $\ln(k) = -1291.5 \times 1/T - 2.7609$ ($R^2 = 0.808$). (b) Reaction rate at different pressure and temperature.
surface and $D_{\text{eff}}$ the effective diffusivity. The value of $D_{\text{eff}} = \epsilon_p D_{\infty}$ is calculated with a catalyst porosity $\epsilon_p = 0.7$ and a tortuosity of $\phi = 7$ which reduces the effective diffusivity by a factor of ten compared to the molecular diffusivity. According to (Losey et al., 2001), the overall external mass transfer coefficient $K_{L a}$ can be calculated by

$$r_{\text{obs}} = \frac{c_{\text{as}}}{K_{L a} + \frac{1}{\eta k_{\text{vol}}}}$$

(5.8)

where $c_{\text{as}}$ is assumed to be the hydrogen concentration in saturated liquid. The calculated residence times in subsection 5.4.1, combined with the recirculation motion in a liquid slug (Wälchli and Rudolf von Rohr, 2006), allow us to safely assume the cyclohexene to be saturated with hydrogen at the entrance of the packed bed. This is calculated by the diffusion length $x = \sqrt{2D_{\infty}t}$, where $D_{\infty}$ is the diffusion coefficient of hydrogen in cyclohexene and $t$ is the diffusion time.

The values obtained in our experiments were in the range of $K_{L a} = 0.8 - 4.2 \text{ s}^{-1}$. Theses values are slightly lower than in the case of (Losey et al., 2001) where 50 $\mu$m particles are used. Nevertheless, they are still 1 – 2 orders of magnitude larger than in laboratory trickle bed reactors.

The internal mass transfer is analyzed by the Weisz criterion

$$\left(\frac{V_p}{A_p}\right)^2 \cdot \frac{r_{\text{obs}} \rho_{\text{app}}}{c_{\text{as}} D_{\text{eff}}} \leq 1.$$  

(5.9)

If Ineq. 5.9 is true, then internal mass transfer can be neglected. The experimental results show a decrease in Weisz modulus from 3 ($p = 6 \text{ bar, } T = 23 \degree C$) to 0.4 ($p = 52 \text{ bar, } T = 75 \degree C$). Therefore, the internal mass transfer is eliminated by increasing pressure and temperature and the reaction is limited by external mass transfer to the catalyst.
5.5 Results of the two phase reaction

In this study we focus on the reaction performance in a packed bed Si/glass microreactor using \( \text{scCO}_2 \) as the reaction solvent where the catalyst is the solid phase and the reaction mixture the liquid of supercritical phase. Mixing of the reactants is carried out on the chip. The supercritical reaction mixture is observed by \textit{in situ} phase studies. The observation of phase behavior for supercritical reaction studies is crucial. A change from a multiphase to a single phase system has significant influence on the heat and mass transfer behavior of the reaction. Therefore, insight in the phase behavior of the reaction mixture at the operating conditions is necessary in order to draw conclusions of the reaction performance. Like in the high pressure three phase study we focus on the hydrogenation of cyclohexene over Pd catalyst.

Standard reaction conditions are 136 bar and 70 °C with volumetric flow rates of \( V_{\text{CO}_2} = 200 \mu L\text{min}^{-1} \), \( V_{\text{C}_6\text{H}_{10}} = 23 \mu L\text{min}^{-1} \) both at 136 bar and 18 °C and \( V_{\text{H}_2} = 5.6 \text{ mLmin}^{-1} \). The ratio of the flow rates corresponds to a molar ratio of \( \text{CO}_2 : \text{C}_6\text{H}_{10} : \text{H}_2 = 90 : 5 : 5 \). The reaction performance is analyzed within temperature and pressure ranges from 40 – 70 °C and 80 – 150 bar, respectively. The \( \text{C}_6\text{H}_{10} : \text{H}_2 \) molar ratio is changed from 1 : 1 up to 1 : 4 for phase studies in order to show the increase of hydrogen solubility in \( \text{scCO}_2 \). Fig. 5.9 shows the reaction formula of the analyzed reaction.

\[
\text{Figure 5.9: } \text{Reaction formula of the catalytic hydrogenation of cyclohexene to cyclohexane using } \text{scCO}_2 \text{ as the reaction solvent.}
\]
5.5.1 Deactivation

Several causes have been discussed for the deactivation of the catalyst during the hydrogenation of cyclohexene. (Watson and Harold, 1993; Arunajatesan et al., 2001) report possible poisoning of the catalyst by peroxide traces in the cyclohexene. Additionally, catalyst leaching and traces of water can reduce the activity of the catalyst. When using $scCO_2$ it is possible that the reverse water gas shift reaction forms $CO$ and $H_2O$ which causes inactivity of the catalyst. Eq. 5.10 shows the water gas shift reaction.

\[ CO + H_2O \rightleftharpoons CO_2 + H_2 \]  \hspace{1cm} (5.10)

![Figure 5.10: Typical evolution of the conversion of cyclohexene during the reaction at $p = 136 \text{ bar}$ and $T = 70 \degree C$ using $scCO_2$ as reaction solvent.](image)

Fig. 5.10 shows the conversion over time of a typical experimental run. Several regions of different conversions can be indicated. First a rise in conversion is observed. After about 90 min maximum conversion was reached in this experiment. It depends on the rate at which the pressure is increased in the system. The residence time at standard conditions is estimated to be in the order of 15 min. This time is normally observed
5.5 Results of the two phase reaction

To reach maximum conversion. The average values of three points at maximum conversion are taken to calculate the reaction rate. Secondly, a slight catalyst deactivation is noticed. This depends on the catalyst efficiency, the possible poisoning, the sintering, the leaching or the fouling during the reaction.

In a third part of the experiment, the cyclohexene flow is stopped after \( t = 232 \text{ min} \) to test for a possible reverse water gas shift reaction. A delay of the reduction of the flow rate can be seen as in the beginning of the experiment.

After \( t = 367 \text{ min} \) the flow is restarted and a similar evolution of the conversion as at the start up is noticed. The conversion does not drop significantly during the time when only hydrogen and scCO\(_2\) flows through the packed microreactor. The intersection of the straight line with the conversion data would indicate the starting value of conversion when CO would be formed and poison the catalyst due to the strong adsorption of CO on active Pd sites. But the conversion reaches the same value than before the stopping of educt flow. This indicates that a possible poisoning by CO can be excluded.

5.5.2 Phase behavior measurements

Traditional method

Phase measurements of mixtures are traditionally performed in high pressure view cells with a volume in the range of several mL. Fig. 5.11 shows a series of photographs through a high pressure view cell of a volume of 2.1 mL. The temperature increase of the isochoric system leads to an increase in pressure. The gas and liquid phase are clearly distinguishable in Fig. 5.11(a). As temperature and pressure increase above the critical point the phase boundary disappears and a single supercritical phase becomes visible (see Fig. 5.11(b)-(e)). The temperature of the transition from sub- to supercritical phase in the experiment is slightly higher than the critical point of CO\(_2\) which is \( T_c = 31 \text{ °C} \). This is due to the mounting of the thermocouple in the wall of the view cell. This leads to a temperature difference of approximately 1 K between the measurement point and the inner wall of the view cell during heating up.
High pressure view cell experiments are difficult to apply when the substances only have small density differences. A homogeneous temperature and concentration distribution in the relatively large volume has to be achieved. We therefore propose in situ phase measurements in the microreactor under continuous flow conditions. The microreactor is placed on an inverse microscope (Axiovert200, Zeiss) and illuminated with a triggered flash lamp for these optical measurements. A new type of microfluidic connections is used for this experiments. To access the upper Si surface for heating, PEEK capillaries (o.d. = 360 µm) were inserted horizontally into open side channels and sealed with epoxy. The high pressure resistivity up to 100 bar is tested for a temperature of maximum 70 °C. Images are taken with a CCD camera (1376 × 1040 pixel²).

The field of view (FOV) $1.78 \times 1.34 \ mm^2$ is achieved with a $5\times$ objective ($NA = 0.12$). For one experiment 200 pictures were taken at 10 Hz with an exposure time of 100 µs. For temperature control a resistive heater foil (Minco) and a resistance thermometer is placed on top of the microreactor. A DC controller regulates the temperature. A scheme of the configuration is seen in Fig. 5.12(a).

This method of image acquisition has some drawbacks compared to fluorescence microscopy as the light reflects from the concave channel bottom (compare Fig. 2.3(a)) and light scattering occurs at phase boundaries. But the main advantage is the possibility to observe the phase behavior of a pure reaction mixture without the addition of dye. Because the influence

**Figure 5.11:** Photograph series of pure CO₂ in a view cell. With increasing pressure and temperature the two phase system change to a supercritical phase and the phase boundary disappears.

**In situ phase measurements**

In situ phase measurements
of the large molecules of fluorescent dyes on the phase behavior is unknown. Besides, precipitation and solubilizing effects could disturb the measurements using laser induced fluorescence. Fig. 5.12(b) shows the location of the different measurement points.

Following downstream direction the fluids undergo different flow regimes and phase changes depending on the location of fluid feed and the microchannel design. A general behavior is observed for all analyzed conditions. At measurement position (1) (see Fig. 5.12(b)) a segmented gas liquid flow of $H_2$ and liquid $C_6H_{10}$ is seen. The gas introduction via a narrow side channel provides a stable formation of gas bubbles and liquid slugs. The gas bubbles reduce and increase size in the subsequent section with the broadening and reducing channel width.

At position (2) dense $CO_2$ is introduced from the side into the segmented gas-liquid flow. The superficial velocities of the merging stream at the $CO_2$ inlet ($p = 136 \text{ bar}, T = 24 ^\circ \text{C}, 90 : 5 : 5$) are $j_{C_6H_{10}} = 0.0053 \text{ ms}^{-1}$, $j_{H_2} = 0.0096 \text{ ms}^{-1}$ and $j_{CO_2} = 0.088 \text{ ms}^{-1}$. These large velocity gradients between $CO_2$ and the passing flow of hydrogen and $C_6H_{10}$ lead to a break up of the well defined segmented flow pattern and an enhanced mixing of the compounds. $H_2$ bubbles and $C_6H_{10}$ slugs are split into small fractions and the reactants start to solubilize in $CO_2$.

Position (3) defines the beginning of the meandering mixing section. It is located 6.6 $mm$ ($= 26 \times d_h$) downstream the $CO_2$ inlet. A bubbly flow of $H_2$ in a liquid mixture of $CO_2$ and $C_6H_{10}$ is observed.

In the meandering mixing section (4) the hydrogen continuously diffuses into the reaction mixture which itself is further mixed.

The fluid passes the sieve with channel widths of 50 $\mu m$ at the entrance of the packed bed (5).

The reaction mixture has a different composition at the outlet (6) due to the reaction in the packed bed. As hydrogen is consumed during reaction the miscibility of the reaction mixture is increased, since lower hydrogen content increases the miscibility of the ternary reaction mixture (Hitzler et al., 1998).
Figure 5.12: (a) Experimental setup for *in situ* phase studies. (b) Measurement positions 1-6 for phase behavior analysis.
5.5 Results of the two phase reaction

Figure 5.13: Typical snapshot images at measurement position 1.
Figure 5.14: Typical snapshot images at measurement position 2.
5.5 Results of the two phase reaction

Figure 5.15: Typical snapshot images at measurement position 3.
Figure 5.16: Typical snapshot images at measurement position 4.
5.5 Results of the two phase reaction

Figure 5.17: Typical snapshot images at measurement position 5.
Figure 5.18: Typical snapshot images at measurement position 6.
Figure 5.19: Micrographs of the reaction mixture in the microfluidic channel using a 20× objective before and after the scCO$_2$ injection (position 2) at 136 bar and 50 °C. The substrate to hydrogen ratio was 1 : 2.

Figs. 5.13-5.18 show typical snapshot images of the phase behavior of the reaction mixture in the microreactor. The pressure is set to $p = 136$ bar. Temperatures are 24 °C and 50 °C, respectively. The substrate to hydrogen ratios are 1 : 1, 1 : 2 and 1 : 4, where the mass flow rate of CO$_2$ is constant at $200 \mu Lmin^{-1}$ (136 bar, 18 °C). Gas-liquid phase boundaries are indicated by dotted lines for better visibility. These pictures describe a qualitative analysis of the phase behavior for the different locations.

Fig. 5.13 shows a stable segmented gas liquid flow. The influence of temperature on segmented gas liquid flow is mainly reflected in the decreasing slug length of C$_6$H$_{10}$ and increasing bubble length of H$_2$ at constant a C$_6$H$_{10}$ : H$_2$ ratio. The bubble length increases with decreasing C$_6$H$_{10}$ : H$_2$ ratio. It exceeds the FOV of the measurement section due to the higher gas flow rate of hydrogen.

Fig. 5.14: The break up of the segmented flow by CO$_2$ is difficult to characterize. The CO$_2$ changes from liquid to a supercritical state from 24 °C to 50 °C. In terms of flow pattern we see no significant change when temperature varies. By decreasing the C$_6$H$_{10}$ : H$_2$ ratio coalesced hydrogen bubbles appear earlier after the injection of CO$_2$.

Fig. 5.19 shows in detail how the two phase flow of H$_2$ and C$_6$H$_{10}$
breaks up by the $scCO_2$ side inlet. Upstream the $CO_2$ inlet $H_2$ bubbles are seen. All $H_2$ is dissolved downstream at the corresponding operating conditions. Large density variations in the fluid occur indicating a strong mixing of the liquid phases.

Fig. 5.15: Hydrogen bubble coalescence appears in downstream position of $CO_2$ injection. Coalesced bubbles occur and form a bubbly flow pattern at $24^\circ C$. A change from $24^\circ C$ to $50^\circ C$ results in the total dissolution of hydrogen in the reaction mixture. With increasing hydrogen content more and larger bubbles are visible at $24^\circ C$. For all $C_6H_{10} : H_2$ ratios there is a single phase flow at $50^\circ C$.

Fig. 5.16: The dissolving of $H_2$ in the reaction mixture proceeds. Disappeared bubbles or decreased bubble sizes were observed at $24^\circ C$ compared to Fig. 5.15. With decreasing $C_6H_{10} : H_2$ ratio more and larger bubbles are present. A single phase flow is observed at $50^\circ C$.

Fig. 5.17: At the inlet to the packed bed most hydrogen is dissolved at $24^\circ C$. Small bubbles are visible at 1 : 2 and 1 : 4. At $50^\circ C$ no change on the previously detected single phase flow is observed. The reaction mixture enters the reaction zone as a single phase at 136 bar and $50^\circ C$ for high hydrogen content such as 9.8 mol%.

Fig. 5.18: At the reactors outlet $H_2$ bubbles are observed only at $24^\circ C$ and a ratio of 1 : 4. In all other cases the hydrogen is entirely dissolved in the reaction mixture due to the complete miscibility of hydrogen in $scCO_2$ (Tsang and Streett, 1981). Additionally, the two effects of an enhanced mixing in the packed bed and the hydrogen consumption increase the homogeneity of the reaction mixture.

At $24^\circ C$ only at high $H_2$ content the mixture was not present in one single phase. This is due to the limited solubility of $H_2$ in the mixture but also to the reduced residence time in the reactor. The mixing time is reduced since more $H_2$ is fed into the microreactor. At $50^\circ C$ no $H_2$ bubbles can be detected within the number of recorded images at the entrance to the packed bed. This leads to the conclusion that the reactants are present in one single phase. At the outlet the reaction mixture contains $CO_2$, $C_6H_{10}$, $C_6H_{12}$ and $H_2$ which is a quaternary mixture, but the critical points of $C_6H_{10}$ ($T_c = 287.3^\circ C$) and $C_6H_{12}$ ($T_c = 280.3^\circ C$) are relatively close together so that the system can be considered as ternary mixture modeled by (Hitzler et al., 1998) using Peng-Robinson equation of state. A single phase behavior of a 90 : 5 : 5
mixture at 120 bar and 50 °C can be derived from their results. (Arunajatesan et al., 2001) conduct phase studies in a high pressure view cell and suggest a homogeneous phase of a 30% converted reaction mixture at about 115 bar and 70 °C. Our experiments show that high hydrogen contents can be dissolved in the reaction mixture using scCO₂ as the reaction solvent. This is not possible in case of a reaction mixture containing only C₆H₁₀ and H₂. If using a Henry constant of \( H = 2648.5 \text{ bar} \) (\( T = 50 \degree \text{C}, p = 136 \text{ bar} \)) (Herskowitz et al., 1983) then H₂ would be soluble in C₆H₁₀ in the extent of \( x = 0.05 \text{ molH}_2/\text{molC}_6\text{H}_{10} \). This low hydrogen solubility results in a two phase flow and often causes mass transfer limitations in three phase catalytic reactions.

5.5.3 Reaction performance

The reactions are conducted at constant flow rate of the reactants \( V_{CO_2} = 200 \mu\text{Lmin}^{-1}, V_{C_6H_{10}} = 23 \mu\text{Lmin}^{-1} \) — both at 136 bar and 18 °C (pump feed conditions) — and \( V_{H_2} = 5.6 \text{ mLmin}^{-1} \). This corresponds to a molar ratio of 90 : 5 : 5. Temperature and pressure in the microreactor are varied in the range of \( T = 40 - 70 \degree \text{C} \) and \( p = 80 - 150 \text{ bar} \) in order to demonstrate the influence of operating conditions on the reaction performance. Optical analysis shows that at constant pressure of 136 bar the reaction mixture is present in a single phase for the observed temperature range. The pressure variation was performed at 50 °C and pressures ranging from 80 – 150 bar. For pressures higher than 100 bar a single phase is present. At 80 bar a two phase flow of H₂ and scCO₂/C₆H₁₀ is observed.

The mean residence time through the packed bed with a measured porosity of \( \epsilon = 0.69 \) is calculated in the range of \( \bar{t} = 0.17 - 0.5 \text{ s} \) depending on the temperature. Isothermal conditions of the microreactor are assumed because of the low Biot number in the order of \( Bi = \alpha L_c/\lambda = 1 \times 10^{-3} \). The observed conversions lay between 20 – 93%, depending on the catalyst loading and operating conditions. The performance of the microreactor is expressed by the converted moles of C₆H₁₀ per time per mass of catalyst.

Fig. 5.20 shows the influence of temperature on the reaction rate. An increase in reaction rate with increasing temperature is obvious.
because of Arrhenius law. The reaction mixture is in single phase for all experiments even at subcritical temperatures of \( \text{CO}_2 \) according to the results of the phase study. At isobaric conditions density, dynamic viscosity and thermal conductivity of the reaction solvent \( \text{CO}_2 \) decrease with increasing temperature. This leads to different observations. The kinematic viscosity, which has a big influence on mass transfer, varies only little in the range from \( 7.4 \times 10^{-8} \, \text{m}^2\text{s}^{-1} \) to \( 8.5 \times 10^{-8} \, \text{m}^2\text{s}^{-1} \). A decrease in thermal conductivity decreases the heat removal from the exothermic reaction. The maximum heat produced by the reaction is \( Q^* = 3.84 \times 10^{-6} \, \text{mols}^{-1} \cdot -118 \, \text{kJmol}^{-1} = -0.45 \, \text{W} \). Appendix B (p. 165) describes the measurement of a lumped heat transfer coefficient from the microreactor surface to the environment (24 \( \text{Wm}^{-2}\text{K}^{-1} \)). Therefore, the heat loss at the surface dominates the heat generation of the reaction above a temperature difference of 11 \( K \) for \( X = 1 \).

Fig. 5.21 shows the dependency of the reaction performance on pressure. No significant change in reaction rate is observed with increasing pressure. Several effects have an important influence on the reaction rate.
5.5 Results of the two phase reaction

Figure 5.21: Pressure vs. reaction rate at $T = 50 \, ^\circ C$. $V_{CO_2} = 200 \, \mu L min^{-1}$, $V_{C_6H_{10}} = 23 \, \mu L min^{-1}$ and $V_{H_2} = 5.6 \, mL min^{-1}$.

when varying the pressure. First, the density of the reaction mixture increases with higher pressure. This means that the diffusion coefficient is lowered. If the reaction was diffusion controlled this would lead to a decrease in reaction rate. Second, the concentration or partial pressure of the involves compounds increase with increasing pressure. This would result in a higher reaction rate with increasing pressure. Additionally, the residence time in the microreactor changes when varying the density of the system.

5.5.4 Mass transfer analysis

A quantitative analysis is necessary to identify possible external mass transfer limitation at the liquid-solid interface. This analysis is difficult to conduct due to the lack of correlations to estimate the mass transfer coefficient in a microscale packed bed. The Thiele modulus and effectiveness factor calculation as performed in the three phase case can not be applied, as no kinetic data is available for the reaction using $scCO_2$ as reaction solvent. The Weisz criterion (Ineq. 5.9) gives an indication
of the limiting step of the pore diffusion limitation. The experiments are analyzed where the conversion is around 20%, at \( p = 136 \text{ bar} \) and \( T = 40 \, ^\circ\text{C} \). In this case, we assume a differential reactor. The bulk concentration of hydrogen is the concentration at the surface of the particles. The molecular diffusion coefficient of hydrogen in \( \text{scCO}_2 \) is estimated at \( 1 \times 10^{-8} \, \text{m}^2\text{s}^{-1} \). This is the order of magnitude reported in different papers e.g. (Baiker and Wandeler, 2001). This value is certainly underestimated. Experiments carried out by (Lüdemann and Chen, 2002) report this diffusion coefficient for \( T = 253 \, \text{K} \) and \( p = 1000 \text{ bar} \). Thus, the Weisz criterion (Ineq. 5.9) is 0.1 for our reaction conditions. This means that the internal mass transfer does not limit the reaction.

### 5.6 Comparison of reactor performance

The efficiency of the presented microreactor in terms of reaction performance is compared to other packed bed reactors at the \( \mu\text{L} \)- and \( \text{mL} \)-scale. We use the space time yield \( (kg_{\text{product}} h^{-1} m_{\text{catalyst}}^{-3}) \) as a benchmark for the hydrogenation of cyclohexene in the case of a three phase reaction and with \( \text{scCO}_2 \) as the reaction solvent. The increase of efficiency in different reactor systems is manifold. Applying high pressure increases the performance because it increases the hydrogen solubility. Using \( \text{scCO}_2 \) as reaction solvent also enhances productivity since the mass transfer resistance from the gas to the liquid phase vanishes in single phase flow. The single phase behavior of the reaction mixture, confirmed by optical measurements, avoids the gas/liquid mass transfer resistance. The concentration of the hydrogen within the single phase is controlled by the flow rate and not by the solubility of hydrogen within the reaction media. The efficiency of the microreactor system is further increased by a good heat removal from the catalyst due to the higher heat capacity of the dense gas and the good thermal conductivity of silicon \((156 \, \text{Wm}^{-1}\text{K}^{-1}, \, T = 300 \, \text{K})\). Tab. 5.1 lists space time yields for different systems found in literature. In case of a three phase reaction the influence of pressure in the investigated pressure range leads to an increase of efficiency of one order of magnitude. The high pressure three phase microreactor has a performance in the same range than the 5 \( \text{mL} \)
reactor at supercritical conditions. The large surface-to-volume ratio of the microreactor combined with the good thermal conductivity of Si leads to an increased heat removal from the exothermic reaction. We show in the present study that the efficiency increases by another order of magnitude compared to the larger reactor at supercritical conditions. This is attributed to the better heat removal, which is obtained in microreactors avoiding hot spots in the packed bed.

Table 5.1: Space time yields (STY) for the solid catalyzed hydrogenation of cyclohexene in different reactors for three phase (*) and two phase reactions with scCO$_2$ as reaction solvent.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Reactor volume</th>
<th>Conditions</th>
<th>Catalyst</th>
<th>STY $[\text{kg}<em>{\text{product}}/\text{h}\cdot\text{m}^3</em>{\text{cat}}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Losey et al., 2001)</td>
<td>3.75 $\mu$L</td>
<td>$\sim 25^\circ\text{C}$</td>
<td>1 – 5% $\text{Pt}/\text{Al}_2\text{O}_3$</td>
<td>7.1 $\times 10^3*$</td>
</tr>
<tr>
<td>(Trachsel et al., 2008)</td>
<td>3.4 $\mu$L</td>
<td>$71^\circ\text{C}$</td>
<td>2% $\text{Pd}/\text{Al}_2\text{O}_3$</td>
<td>2.6 $\times 10^5*$</td>
</tr>
<tr>
<td>(Hitzler et al., 1998)</td>
<td>5 mL</td>
<td>$340^\circ\text{C}$</td>
<td>5% $\text{Pd}/\text{Deloxan}$</td>
<td>2.5 $\times 10^5$</td>
</tr>
<tr>
<td>present study</td>
<td>3.8 $\mu$L</td>
<td>$70^\circ\text{C}$</td>
<td>2% $\text{Pd}/\text{Al}_2\text{O}_3$</td>
<td>1.5 $\times 10^6$</td>
</tr>
</tbody>
</table>

5.7 Conclusions and summary

We present a chip based Si/glass packed bed microreactor for high pressure three and two phase reactions. The hydrogenation of cyclohexene over $\text{Pd}/\text{Al}_2\text{O}_3$ catalyst is studied as a model reaction. All reactants
are brought in contact, mix and react on the chip. First, the three phase gas-liquid-solid hydrogenation reaction is conducted in the packed bed microreactor. Segmented gas-liquid flow is identified as flow pattern and the reaction rates at different operating conditions are analyzed. A mass transfer analysis and comparison with batch experiments indicate a limitation of the reaction by external mass transfer.

In a second project, $scCO_2$ as reaction solvent is used to further decrease mass transfer resistance. *In situ* phase studies of the reaction mixture and the reaction performance are discussed. The phase studies confirm a single phase reaction mixture at 25 °C and 50 °C during isobaric reaction conditions of 136 bar. The reaction performance increases with temperature whereas no significant increase is observed with increasing pressure. A comparison of the reactor performance in terms of space time yield with different reactor systems for the same model reaction is presented. The results indicate that high pressure microreactors are favorable for exothermic reactions because of the good heat removal due to the small reactor length scales. The space time yield is one order of magnitude greater than earlier reported values.

This study shows the feasibility of high pressure Si/glass microreactors for reactions using $scCO_2$ as the reaction solvent. The concept of an integrated high pressure microreactor chip is used for future *in situ* spectroscopic measurements. Further studies will investigate *in situ* spectroscopic analysis methods as UV/Vis and Raman which will provide deeper insights in high pressure heterogeneous reactions involving supercritical fluids (see section 6.2.1).
Chapter 6

Summary and Outlook

6.1 Summary

This thesis presents the design of a microreactor for reaction using \( \text{scCO}_2 \) as reaction solvent. The microfluidic design and fabrication process of such a microreactor is strongly linked to the mechanical strength of the involved materials and microfluidic connections to withstand pressures up to 140 bar and temperatures up to 80 °C. The requirement of micromachinability and optical access into the reaction channel for \textit{in situ} measurements suggests to use silicon and glass as reactor material. The Si/glass microreactor is fabricated using photolithography, dry etching and anodic bonding techniques. Special attention is paid to the microfluidic connection which connects the microreactor with its macroscale environment. The environment consists of pumps, tubing and valves. Integrated connections are developed by soldering stainless steel capillary onto the inlets and outlet of the microfluidic chip. The microreactor is characterized in terms of mechanical, fluid dynamic and chemical reaction engineering aspects. The hydrogenation of cyclohexene to cyclohexane over Pd catalyst is performed as model reaction at high pressure. The case of a three phase gas-liquid-solid reaction and a two phase SCF-solid
reaction using \( scCO_2 \) as reaction solvent are analyzed. Commercially available catalyst particles are used as catalyst substrate in the form of a packed bed. Optical access into the reaction channel is ensured.

A mechanical analysis of the microreactor under high pressure and temperature conditions is performed. Tensile tests of the microfluidic connections, pressure burst tests of the device and an analytical examination is conducted. The results show that the microfluidic connections have a high mechanical strength exceeding the applied pressure on the Si/glass device. The width of the microchannel is a crucial parameter and the maximum applicable pressure depends inversely on the square of the channel width. The maximum open width of the microchannel is therefore set to a value of 400 \( \mu m \). The operating temperature at high pressures is limited since the coefficients of thermal expansion of solder and Si differ. The microreactor is tested successfully over 8 \( h \) at 140 \( bar \) and 80 \( ^\circ C \) without failure.

The hydrodynamics and phase distribution in segmented gas liquid flow is experimentally analyzed in a fluid dynamic characterization of the microreactor. The pressure drop measurements at single and two phase conditions in an empty and packed bed microchannel show that the standard equations for friction factor and the Ergun equation are applicable. Residence time distribution is measured and compared at different flow rates. The mean liquid residence time is mainly defined by the liquid flow rate where the gas flow rate has a minor influence. Particles and the increase of the gas content in the two phase flow enhance dispersion.

In segmented gas-liquid flow the formation of a thin liquid film around a gas bubble is observed through which neighboring liquid slugs communicate. The size of this films in the corner and at the wall of the rectangular microfluidic channel is measured by confocal laser scanning microscopy. The corner films have a nearly constant size for \( Ca < 10^{-2} \) of 0.09 \( d_h \). The wall film thickness turns out to be about 0.02 \( d_h \) in size. The total film cross section covers about 10% of the channel cross section, whereas the corners are about 70% of the total film area. Because of these results, the flow rates are kept as low as possible to
reduce dispersion and bypassing of the liquid in the higher porosity regions of the packed bed at the channel walls. For the lower limit of flow rates also the error and ranges of the experimental setup has to be taken into account.

As a model reaction the catalytic hydrogenation of cyclohexene is analyzed at high pressure and temperature in the packed bed microreactor. The microfluidic channel design is adapted that mixing of the reactants and the reaction is carried out on chip and a observation of the flow is achieved. The three phase gas-liquid-solid reaction is performed at pressures up to 50 bar and temperatures up to 70 °C. A mass transfer analysis shows that the reaction is limited by external mass transfer of hydrogen to the catalysts active sites. Mass transfer coefficients are calculated that are comparable to values found in literature. To further decrease mass transfer resistance, \( \text{scCO}_2 \) is added as reaction solvent to provide a single phase flow of the reaction mixture. Experiments are conducted at pressures up to 150 bar and 100 °C. An increase in observed reaction rate indicates a drastically reduction in mass transfer limitation. The reaction performance compared to other micro- and macroscale reactors is increased by one order of magnitude. Instead of using a high pressure view cell the phase behavior of the reaction mixture under \( \text{scCO}_2 \) conditions is analyzed \textit{in situ} at 136 bar. Single phase behavior is observed even at low temperatures of 24 °C. Increasing temperature leads to an enhanced solubility of hydrogen up to a molar ratio of 87.5 : 10 : 2.5 \((\text{CO}_2 : \text{H}_2 : \text{C}_6\text{H}_{10}) \).

6.2 Outlook

6.2.1 \textit{In situ} analysis of reactions

The goal of a micro total analysis system (\( \mu \)TAS) has still not been reached. This project contributes to this idea by a microfluidic chemical analysis system for high pressure and high temperature that offers fast and \textit{in situ} optical observations of heterogeneously catalyzed reactions.
In future studies, the focus should be on \textit{in situ} detection methods for continuous high pressure and high temperature reactions.

Several \textit{in situ} detection methods exist for monitoring e.g. chemical reactions online in a microfluidic device (Schwarz and Hauser, 2001; Viskari and Landers, 2006). Fluorescence is widely used to characterize mixing and the detection of fluorescent labeled molecules in small concentrations. Infrared detection offers the possibility to monitor the formation of chemical species during reactions (Herzig-Marx et al., 2004). The method is limited by the availability of IR-transparent material in the longer wavelength spectrum. In our study we use the presented microreactor setup and Raman spectroscopy to point out the advantages of the well defined and controllable reaction conditions and the optical access into the Si/glass microreactor at high pressures.

\textbf{In situ online Raman spectroscopy}

Raman spectroscopy is a well-established analytical method where molecules are excited by a monochromatic laser source and emit energy according to the Stokes and anti-Stokes Raman scattering effect from virtual energy levels of the electrons. Since Raman scattering is very specific for chemical bonds in molecules. A ”fingerprint”of the molecule can be measured. Raman scattering is a very weak phenomenon. Therefore, we have to be careful when choosing the exciting wavelength in a range where no fluorescence of the analyzed species occur which would overlap with the Raman signal.

The presented microreactor offers the possibility to analyze the reaction species of the heterogeneously catalyzed model reaction \textit{in situ} and in real time on the chip. In high pressure chemical reactions this continuous flow microreactor provides new insights in the forming of transition products and reactions on the catalyst surface without the need of heavy macroscale high pressure equipment and the therefore needed extended safety precautions. The reduced sample volume enables the monitoring of reactions under well defined conditions in terms of temperature, pressure and mixing.
To demonstrate the feasibility of the high pressure microreactor system for \textit{in situ} online Raman spectroscopy the microreactor is operated at a pressure of 100 bar. The temperature is controlled by a resistive heating at 25 and 40 °C. Raman spectra are acquired using an Ocean Optics QE65000 spectrometer with a RIP-RPB fiber optic probe with a focal length of 7.5 mm placed in front of the microreactor. A continuous wave laser at a wavelength of 785 nm with 500 mW power serves as the light source. The spectra are accumulated for 7 s. Fig. 6.1 shows a scheme of the microreactor and the corresponding measured Raman spectra at different measurement locations.

First the fluid inlets are analyzed. The cyclohexene inlet shows good agreement with a reference measurement where a characteristic band is at 820 cm\(^{-1}\). A higher fluorescence signal is recognized in the microreactor at higher wavenumbers possibly from the microreactor material Si and glass. At the CO\(_2\) inlet measurement at 298 K and 313 K were taken. The two characteristic peaks for CO\(_2\) symmetric stretching are observed at 298 K. An additional C\(_6\)H\(_{10}\) signal appears at higher temperatures. This can be attributed to the increased diffusivity of organic solvents in CO\(_2\) when it is undergoing the transition to a supercritical state and a certain backmixing occurs. Another explanation of the appearance of reactant in the CO\(_2\) inlet could be that there is a pulsating flow formed due to the high density fluctuations near the critical point of CO\(_2\). This leads to a periodic appearance of reactant in the inlet which is averaged over the sampling time.

No product is detected at the position before the catalyst bed. The Raman spectra show the characteristic peak of the reference measurement of cyclohexene. After the catalyst bed the characteristic peak of the product cyclohexane is appearing indicating the hydrogenation of cyclohexene over the Pd catalyst particles. We see that the intensity and therefore the concentration of product increases with increasing temperature. It has to be stated that the molar ratio of the reaction mixture is 90 : 5 : 5 (CO\(_2\) : H\(_2\) : C\(_6\)H\(_{10}\)) and even for high CO\(_2\) content small concentrations of reactant and product can be resolved. The analysis of the product evolution in the packed bed can not be carried out since the laser power is too high. The strong absorption of the laser light on
Figure 6.1: Online Raman spectroscopy measurement of the hydrogenation of cyclohexene in \textit{sc}CO$_2$ at 100 bar.
the catalyst burns the particles during the measurement process. In further studies the laser intensity should be decreased by an attenuator to observe the concentration distribution of reactants and product in the packed bed in detail.

This first example of in situ online Raman detection in a high pressure Si/glass microreactor gives an idea of the manifold possibilities of reaction analysis which can be performed in the presented system. High pressure reactions which have to be conducted under heavy safety precautions can be easily performed continuously at the micro scale without any danger. The very fast temporal response on changes in flow rates, system pressure and reactor temperature makes the microreactor and its high pressure setup favorable for cycling experiments. Compared to batch reactions the microreactor experiments are less time consuming.

### 6.2.2 Expanding range of operating conditions

The microscale dimension of the microreactor enables the device to operate at high pressures. The operating temperature is limited to about 100 °C at a pressure of 150 bar. To study a wider range chemical reactions under supercritical conditions the temperature and pressure range should be expanded. This requires the choice of mechanically stable material for the microfluidic connections with coefficients of thermal expansion within the same range in order to minimize thermal loads.

**Water as supercritical solvent**

Apart from CO₂ other supercritical solvents can be used. Water with a critical point of $T_c = 374.0$ °C and $p_c = 220.6$ bar is used in supercritical water oxidation (SCWO) for toxic waste treatment. The major drawback of present SCWO systems is the high energy consumption and the demanding safety precautions at high pressure and high temperature operating conditions. This inhibits a wide spread of SCWO process plants in chemical industry. The combinations of supercritical water and microreactors offers interesting possibilities in reducing energy consumption and safety demands in SCWO. (Kawanami et al., 2007) present a
microfluidic system for the rapid $C - C$ coupling in high pressure and high temperature water. Even the supercritical point of water is not exceeded in this study feasibility, low energy consumption and the easy of handling are well demonstrated.

New reaction classes

This thesis studies the feasibility of the combination of microreactors and supercritical fluids in the case of a model reaction. In future studies the focus should be on new reaction classes which are difficult to conduct in conventional reactor systems. One example is the $CO_2$ fixation. The knowledge about the environmental impact of $CO_2$ as major greenhouse gas has been increased in the last years and ways for its reduction in the atmosphere are being investigated. One possibility is the $CO_2$ fixation at high pressure, where $CO_2$ is directly hydrogenated to formic acid derivatives (Urakawa et al., 2007). Formic acid is then used as base chemical. The hydrogenation is difficult to handle in a continuous solid catalyzed process which would be necessary to convert large amount of $CO_2$. Precise temperature control and short residence times are necessary for optimal reaction conditions. Both can be achieved in a microreactor system which makes it a valuable tool to understand the chemical mechanisms.

Solder glass Kovar microfluidic connections

A possible approach is the use of solder glass and Kovar to realize an integrated microfluidic connection on a Si/glass chip. Solder glass is a lead containing low temperature melting glass which is used for hermetic sealing of sensors and optical fibers with Kovar, glass or other materials. Kovar (Fe54Ni29Co17) is an alloy which matches the thermal expansion coefficient of glass. In several experiments we used pressed solder glass preforms (Diemat Inc., Byfield, US) and glass granulate (G018-174, Schott Electronic Packaging, Germany) as solder and Kovar capillaries with an o.d. of 1.6 mm to fabricate an integrated microfluidic connection.
The solder glass is heated up to a temperature of 420 °C, held for 30 min and then slowly cooled down to minimize thermal stress in the joining materials. A vacuum chamber with a halogen lamp as heat source is used. Because during the melting of the solder binder material gases out, vacuum is necessary to avoid the forming of void in the solder joint. The control of the halogen lamp by a DC controller enables a precise temperature control up to 500 °C. The Si/glass microreactor is placed on top of the heat source and the capillary is hold in place by a special fixture. When solder glass granulate is used a mould fabricated of Kovar is placed around the inlet and the capillary. During the fabrication the filled granulate melts and forms a joint with the capillary, the mould and the Si surface. Using pressed preforms no mould is needed.

Fig. 6.2(a) shows the experimental setup for the fabrication of microfluidic connections using solder glass and Kovar. Fig. 6.2(b) represents the temperature above the light source during heating up. The process temperature of 420 °C is reached within 30 s. In an evacuated chamber the temperature rise is decreased compared to the non evacuated case due to the inexistent convective heat transfer to the temperature sensor.

**Figure 6.2:** Solder glass microfluidic connection fabrication. (a) Photograph of the vacuum chamber with inserted halogen lamp as heat source and temperature controller. (b) Temporal temperature evolution of the heat source in case of an evacuated and non evacuated chamber.

The fabricated solder glass specimens are tested in tensile test (see section 3.1) and compared to microfluidic connections realized with epoxy
adhesive as joint material.

**Figure 6.3:** Averaged maximum force of tensile test for solder glass and epoxy microfluidic connections. A series of 5 specimen was tested each. Error bars indicate minimal and maximal deviation from the mean value.

Fig 6.3 shows the averaged maximum tensile force from tensile tests. A mean pull out force of 68.2 N for the solder glass and 300.7 N for the epoxy is measured. This corresponds to a theoretical pressure (Eq. 3.3) of 339 bar and 1496 bar, respectively. The solder glass specimens fail by the separation from the Si surface and show a certain amount of voids in the glass joint. As comparison the epoxy connections fail due to pull out of the capillary and show relatively high pull out forces. Such epoxy based connections could not be used in high temperatures and in combination with solvents, since even high performance structural epoxy adhesive has a limited temperature and chemical resistance. The results show that further improvement of the solder glass microfluidic connection fabrication process is necessary in order to obtain void free connections of high reliability.

**Modular microfluidic connection**

To realize a versatile and easy to handle online analytical system for high pressure and high temperature reactions a modular connection
system for the Si/glass chips would be favorable. An easy exchange of different microreactor designs and catalyst would be the major advantages. The most challenging part would be the realization of a press sealing for high pressures and temperatures which does not apply any tension on the chip. Too high or uneven stress distribution on the chip would introduce loads under which the microreactor breaks.


Appendix A

All cleanroom fabrication processes are described for the ETH D-MAVT cleanrooms and the equipment in the CLA building at ETH Zentrum.

Wafers supply

Si wafers used are 100 mm diameter, p/Boron type, ⟨100⟩ oriented, double side polished with an average resistivity of 15 Ωcm and 500 µm thickness (Si-Mat Silicon Materials, Landsberg am Lech, Germany). Glass wafers used are 100 mm diameter, Borofloat®, double side polished, 700 µm thickness (Mark Optics, Santa Ana, USA).

Photolithography recipe

Si Wafer are used as delivered. The wafers are cleaned for 10 min in an oxygen plasma (TePla 300 E) at a pressure of about 0.1 mbar. The adhesion of the photoresist is improved by a Hexamethyldisilazan (HMDS) treatment with a 5 min nitrogen purge, 1 min HMDS treatment followed by an additional 5 min nitrogen purge. The wafer is then loaded on a spin coater (CT60, Suss MicroTec, Garching, Germany). As positive photoresist AZ4562 (MicroChemicals GmbH, Ulm, Germany) is used. 3.3 mL of AZ4562 is poured on the middle of the wafer and the
The spin coating sequence is started. The program consists of a first cycle for 5 s at 700 rpm with an acceleration of 500 rpms$^{-1}$ and a second cycle for 35 s at 1700 rpm with an acceleration of 1000 rpms$^{-1}$. The procedure results in a 10 µm thick layer of photoresist. The wafer is prebaked prior to illumination for 12 min on a hotplate at 90 °C. The wafer is illuminated on a maskaligner (MA6, Suss MicroTec, Garching, Germany) with a 350 W Hg bulb with a spectra of 250 - 400 nm. The intensity of the lamp on the mask is about 12 mWcm$^{-2}$. The photoresist has to be illuminated with an intensity of 696 mJcm$^{-2}$. The parameters are set as follows: exposure time is about 50 s (depending on the actual intensity of the bulb), alignment gap 50 µm and soft exposure type.

The microreactor design is printed on a transparency foil by a high resolution printer (2400 dpi) by Grossen Satz, Zürich. The foil is cut and placed on a glass plate and used as a photolithographic mask. The glass plate is cleaned with acetone and isopropanol, the foil with isopropanol. Prior to the loading wafer and mask are cleaned with nitrogen.

After illumination the wafer is developed in a solution of a volumetric ratio of 1:4 (Microposit 351 developer:DI water) (Shipley Company, Marlborough, USA) for 3 min and rinsed in DI water for 3 min. The wafer is dried with nitrogen.

**Wafer cleaning**

Si wafers are cleaned from photoresist with acetone in an ultrasonic bath for 12 min followed by 12 min in isopropanol. The wafers subsequently are rinsed in a quick dump rinser until the resistivity of the waste water is higher than 14 MΩcm. The wafers then are dried in a spin rinser dryer (SRD, Semitool, USA). The cleaning is finished by an oxygen plasma treatment for 10 min.
Dry etching

The dry etching is performed on an Inductive Coupled Plasma Etching System (ICP) (Surface Technology Systems STS, Newport, UK). The process consists of an etch cycle followed by a passivation cycle. Prior to use the system is cleaned by an oxygen plasma for 30 min. The etch rate is $\sim 1.5 \mu m$ per etch cycle resulting in a rectangular channel shape with a slightly concave channel bottom and slight scalloping at the channel walls. Tab. 6.1 shows the values of the process parameters for the dry etching.

Table 6.1: ICP process parameter settings.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Etch cycle</th>
<th>Passivation cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cycle time</td>
<td>16 s</td>
<td>6 s</td>
</tr>
<tr>
<td>$C_4F_8$ flow</td>
<td>40 sccm</td>
<td>100 sccm</td>
</tr>
<tr>
<td>$SF_6$ flow</td>
<td>130 sccm</td>
<td>0 sccm</td>
</tr>
<tr>
<td>$O_2$ flow</td>
<td>13 sccm</td>
<td>0 sccm</td>
</tr>
<tr>
<td>RF power</td>
<td>1000 W</td>
<td>800 W</td>
</tr>
<tr>
<td>Platten power</td>
<td>100 W</td>
<td>0 W</td>
</tr>
<tr>
<td>Base pressure</td>
<td>0.001 mbar</td>
<td></td>
</tr>
<tr>
<td>Chuck temperature</td>
<td>15°C</td>
<td></td>
</tr>
<tr>
<td>Max. He leakrate</td>
<td>0.019 mbarmin$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Valve position</td>
<td>40%</td>
<td></td>
</tr>
</tbody>
</table>

For back side etching a dummy Si wafer is attached onto the already etched wafer side with white wax at a temperature of about $T = 50 ^\circ C$ on a hotplate.

Anodic bonding

The anodic bonding of Si and glass is performed on a SB6 substrate bonder (SUSS MicroTec AG, Garching, Germany). The Si wafer are
cleaned according to the cleaning procedure described above. Glass wafers as supplied are cleaned in oxygen plasma for 10\textit{ min}. The wafers are cleaned with nitrogen prior to loading. The settings for the bonding process are as follows: Bottom temperature 450 °C, Voltage 1500 V, Tool pressure 90 N. The process is stopped when the measured current is decreased below a value of 0.15 A. This process usually takes about 20 \textit{min}.

\textbf{Lift-off process}

The negative photoresist NR7-1000P (Futurrex, Inc., Franklin, USA) is used for the patterning of the Si wafer for subsequent evaporation of metal films. The wafer is cleaned with the standard procedure and treated with HMDS as described above. 3.3 mL of photoresist is spun onto the wafer. A prebake at 150 °C for 30 s is performed. The exposure time on the MA6 is about 50 s corresponding to an intensity of 7 mW cm\textsuperscript{-2}. A postbake at 100 °C for 3 \textit{min} is done. The photoresist is developed in 4:1 (RD6:DI water) (Futurrex, Inc., Franklin, USA) for 2 \textit{min} and afterwards rinsed well in DI water for 3 \textit{min}. After evaporation of the metal films the photoresist is removed with RR4 (Futurrex, Inc., Franklin, USA) for 5 \textit{min} and rinsed with DI water for 3 \textit{min}.

\textbf{SU-8 thick photolithography process}

The Si wafer are dehydrated for 5 \textit{min} on a hotplate at 200 °C. The spin coating of 4 mL SU-8 50 (MicroChem Corp., Newton, USA) is performed with following settings: 5 s at 500 rpm (100 rpms\textsuperscript{-1} acceleration) and 30 s 1000 rpm (300 rpms\textsuperscript{-1} acceleration). At room temperature the coating is settled down on a leveled plate for 20 \textit{min}. We prebake the wafer at 65 °C for 20 \textit{min}. A second spin process as described leads to an approximate thickness of 300 \textmu m. The softbake parameters performed on a leveled hotplate are as follows: 5 \textit{min} at 65 °C, 5 \textit{min} at 75 °C, 5 \textit{min} at 85 °C, 30 \textit{min} at 95 °C, 5 \textit{min} at 65 °C, 10 \textit{min} at room temperature. The exposure time on the
MA6 is about 50 s, calculated from the actual intensity of the bulb and the needed energy of 400 Jcm\(^{-2}\).

The hardbake parameters performed on a leveled hotplate are as follows: 10 min at 65 °C, 10 min at 80 °C, 10 min at 90 °C, 20 min at 100 °C, 5 min at 65 °C, 10 min at room temperature.

The development is done for 20 min in MR Dev 600 (Micro Resist Technology GmbH, Berlin, Germany). Afterwards the wafer is rinsed with isopropanol and DI water and carefully dried with nitrogen.

PDMS soft lithography process

The SU-8 master is cleaned from particles with air and silanized with Trichloro(1H,1H,2H,2H-perfluorooctyl)silane (Sigma-Aldrich, Buchs, Switzerland) in a desiccator at a pressure below 1 mbar for 45 min. Polydimethylsiloxane (PDMS) (Sylgard® 184, Dow Corning, Wiesbaden, Germany) base and curing agent are well mixed in a weight ratio of 10:1 in a cup. The PDMS is degassed in a desiccator for 60 min at a pressure below 1 mbar. The PDMS is then poured over the master and cured for 2 h at 70 °C in an oven.

After curing the PDMS is carefully peeled off the master and cut into the according size to fit the glass cover slides. PDMS and glass cover slides are five times cleaned with Scotch® tape (Magic® TM, 3M, Rüschlikon, Schweiz). Inlet and outlet holes are made with a puncher to fit the 1.56 mm o.d. PEEK tubing. Inlet and outlet holes were carefully cleaned to remove possible residuals from the punching.

The to be bonded surfaces are treated in an oxygen plasma cleaner (PDC-32G-2, Harrick Plasma, Ithaca, USA) with a RF coil power of 18 W for 45 s. Laboratory air is used as oxygen source. After the plasma treatment PDMS and glass cover slide are sealed together. 40 mm long PEEK tubings are cut and cleaned with isopropanol and afterwards attached into the corresponding inlet and outlet holes. A 45 s plasma treatment is done as described above. Epoxy glue resin and hardener (Devcon® 5 Minute® Epoxy, Devcon, Danvers, USA) are 1:1 mixed in a cup for 1 min and then applied on the microfluidic connections. The epoxy is cured over night at 70 °C in an oven.
Microfluidic connection fabrication

First, stainless steel capillaries (SS 316, o.d. = 1.59 mm, i.d. = 0.5 mm) are cut in 5 mm long pieces, turned at one end (45 °, 0.45 mm) and grinded at a length of approximately 8 mm. The capillaries are washed with acetone and dried with air. The grinded area is coated with flux agent F-611-INOX (Fontargen, Eisenberg, Germany) and pre-tin-plated with the silver tin based solder A-611 (Fontargen, Eisenberg, Germany). The soldering iron is set to a temperature of \( T = 450 ^\circ C \). The capillaries are then cleaned in hot water.

The Si/glass microreactor is prepared as follows prior to the evaporation of the metallic pads around the inlet and outlet holes. The Si surface is cleaned with ethanol a cleaning agent Balzers Substratreiniger 1 (OC Oerlikon Balzers AG, Balzers, Lichtenstein) and isopropanol. The chips are dehydrated in an oven at 200 °C for 10 min. The chips are fixed on an alumina shadow mask and the metallic layers are subsequently deposited by electron beam evaporation in a Pfeiffer Vacuum Classic 500 PVD system (Pfeiffer Vacuum GmbH, Asslar, Germany).

To solder the microfluidic connections a drill chuck to fix the capillaries and a positioning table with a hotplate is used. An elastic guidance is used to slightly press down the capillary in the corresponding inlet/outlet hole. The hot plate is set to \( T = 160 ^\circ C \) and a soldering iron to \( T = 350 ^\circ C \). The capillary and the microreactor are positioned in the drill chuck and on the hotplate, respectively. The metallic pad and the capillary are coated with flux agent F-611 (Fontargen, Eisenberg, Germany) and soldered with A-611 (Fontargen, Eisenberg, Germany). After all capillaries are attached, the microreactor is cooled down and cleaned from flux agent in hot water.

Polishing

The sample is cut by wire dicing and then polished with slurries of stepwise reducing particles sizes. The particle sizes are chosen as
follows: 1200 $\mu m$ SiC, 6 $\mu m$ diamond, 3 $\mu m$ diamond, 1 $\mu m$ diamond and 0.25 $\mu m$ diamond.
Appendix B

The thermal analysis of the microreactor is performed in terms of the heat transfer from and to the microreactor.

The microreactor is assumed to have an uniform temperature distribution because of its small Bi number.

\[ Bi = \frac{\text{heat flux by convection}}{\text{heat flux by conduction}} = \frac{\alpha L_c}{\lambda} \ll 1 \]  \hspace{1cm} (6.1)

where \( \alpha \) is the heat transfer coefficient from the reactor to the environment, \( L_c \) the characteristic length of the microreactor and \( \lambda \) the thermal conductivity.

To ensure isothermal conditions in the microreactor during the exothermic reaction the heat transfer coefficient has to be sufficiently high to remove the heat of reaction. We focus on the heat transfer from the microreactor to the environment since the heat transfer coefficient from the fluid to the channel wall is orders of magnitude higher (in the range of \( 10^4 \text{ Wm}^{-2}\text{K}^{-1} \) (Li et al., 2004)) and therefore not the limiting heat transfer resistance.

To calculate a lumped heat transfer coefficient \( \alpha_l \) the microreactor is heated up by resistive heating and then cooled down with no power input. Water at different flow rates is fed through the microchannel.

The energy balance considering only internal energy is
\[
\frac{\partial E}{\partial t} = Q_{in}^* - Q_{out}^* + Q_{source}^* = 0
\] (6.2)

\[
\frac{\partial}{\partial t} (M c_p T) = -A \alpha \cdot (T - T_\infty)
\] (6.3)

with \(E\) the total energy and \(Q_i^*\) the heat power. \(M\) is the mass of the microreactor, \(c_p\) the heat capacity and \(T\) the temperature of the microreactor. The differential equation derived from 6.3 is

\[
\frac{\partial T}{\partial t} = -\frac{A \alpha}{M c_p} \cdot (T - T_\infty)
\] (6.4)

substituting \((T - T_\infty) = \theta\)

\[
\frac{\partial \theta}{\partial t} = -\frac{A \alpha}{M c_p} \cdot \theta
\] (6.5)

This leads to the temperature profile of the cooled down microreactor following the equation

\[
\theta(t) = \theta_i \cdot e^{-\frac{A \alpha}{M c_p} t}
\] (6.6)

or

\[
\frac{T - T_\infty}{T_i - T_\infty} = e^{-\frac{A \alpha}{M c_p} t} = e^{-t/\tau}
\] (6.7)

with \(\tau\) the time constant \(\frac{M c_p}{A \alpha}\).

Fig. 6.4 shows the decrease in surface temperature measured with a thermocouple on the Si surface at the reactor outlet. No significant change of the cooling characteristic is seen with increasing flow rate. This leads to the conclusion that most of the heat is dissipated by the
natural convection and not by convection in the microchannel. The mean value of $\alpha_l$ can be calculated using Eq. 6.7 and is $24 \, Wm^{-2}K^{-1}$ based on the microreactor surface. The weight and $c_p$ of the reactor was calculated by weighting the different materials (Si, glass, solder, steel capillaries) according to their mass.

The heat produced by the reaction (23 $\mu$Lmin$^{-1}$ cyclohexene feed, $X = 1$) is 0.45 $W$. With the lumped heat transfer coefficient a temperature difference of 10.6 $K$ to the environment is needed to dissipate the generated heat by the reaction. If the reactor is placed in a stirred bath for temperature control the heat transfer coefficient is even higher and the heat is removed with a lower temperature gradient.
Curriculum Vitae

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