Novel Multiphase Chemical Reaction Systems Enabled by Microfabrication Technology

By

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Abstract

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Advances in MEMS (micro-electromechanical systems) have enabled some of the "Lab-on-a-Chip" technologies and microfluidics that are pervasive in many of the current developments in analytical chemistry and molecular biology. Coinciding with this effort in micro-analyticals has been research in chemical process miniaturization -- reducing the characteristic length scale of the unit operation to improve heat and mass transfer, and ultimately process performance. My research has involved the design and fabrication of novel chemical reaction systems using MEMS and microfabrication methods (photolithography, deep-reactive-ion etching, thin-film growth and deposition, and multiple wafer bonding). Miniature chemical systems provide the opportunity for distributed, on-demand manufacturing, which would eliminate the hazards of transportation and storage of toxic or hazardous chemical intermediates. Reactions that are particularly suitable for miniaturized chemical systems are those that are fast and involve toxic intermediates: the controlled synthesis of phosgene is such a reaction and has been demonstrated in a microfabricated packed bed reactor. Owing to the high surface-to-volume ratios, micro chemical systems also have the potential to make improvements in process performance through enhanced heat and mass transfer. Heterogeneously catalyzed gas-liquid reactions have been performed in the microfabricated reactors and have been shown to have mass transfer coefficients several orders of magnitude larger than their industrial-scale counterparts. Multiphase reactions are often hindered by mass-transfer limitations owing to the difficulty in transporting the gaseous reactant through the liquid to the catalytic surface. The microchemical device has been designed to increase the interfacial gas-liquid contacting area by promoting dispersion and preventing coalescence. Microfabrication allows the design of reactors with complicated fluidic distribution networks, staggered arrays of microstructural features to promote mixing, and the integration of sensing and temperature control. Other uses of microfabrication include the incorporation of porous silicon as a high surface area catalyst support. In all, performing multiphase chemistry on a chip has been demonstrated to have inherent advantages, particularly for those fast reactions that can benefit from improved mixing and mass transfer.
Acknowledgements

Before I acknowledge all of the people at MIT, I must begin by acknowledging the support of my parents, Bob and Diane Losey. This thesis is the result of their continued encouragement and support. Their lifelong commitment to the values of education, honesty, and hard work, has been the cornerstone upon which this thesis was built. This thesis is dedicated to both of them.

Every good thesis starts with a good advisor. I could not have asked for a better advisor than Klavs Jensen. We have enjoyed a remarkable working relationship and I have thoroughly enjoyed the research that we have crafted together. It’s a shame that there isn’t enough time in a day to try out all of the ideas that we came up with throughout this thesis. Fortunately, at least one of the ideas (this thesis) turned out to be a legitimate one. I am grateful for the confidence that he has repeatedly placed in me and I am deeply indebted for his advisement and mentorship.

Also, I am also extremely fortunate to have had Marty Schmidt as an advisor for this thesis. The collaboration between Marty and Klavs is truly a unique opportunity, blending the best of MEMS design and chemical engineering. If it were not for Marty’s grounding in practicality and sensible design, many of us would still be in the clean room. It was truly valuable and immensely enjoyable to have Marty’s involvement.

The efforts of the other members of my thesis committee, Professors Daniel Blankschtein and Paul Laibinis are gratefully acknowledged. Their involvement, flexibility, and time committed were greatly appreciated.

Collaboration with industrial partners provided a valuable resource for technical guidance and understanding of traditional multiphase reactor design. This research was funded in part by an industrial sponsor. That company, through the efforts of Denise Anderson, deserves credit for their foresight and commitment to academic research. Their sustained interest in the results of this work, while limiting direct involvement, was a source of continued inspiration. The value of having Denise Anderson as a source of feedback and technical guidance can not be over-stated.

And I would like to offer my sincere thanks to the personnel of the Microsystems Technology Lab (MTL). Their expertise, patience, and commitment to the education of the students has made our research possible. I would like to thank MIT’s Felice Frankel for numerous photographs which have appeared in many of our publications and in this thesis. There are a number of other resources throughout MIT that I relied upon throughout my research. The people whose help has been instrumental include Fred Cote of the Edgerton Center student machine shop, Andrew Gallant of the MIT Central machine, and Tony Garrett-Reed of the Materials Science Microscopy Lab.

Lastly, I want to thank all of my friends and fellow students at MIT who have been incredible role-models and sources of support. One in particular, Dr. Laura Pruette, to whom I am forever indebted for her love and support.
The following acknowledgements are related directly to the work involved with this thesis.

The initial single-channel reactor design was motivated by the liquid mixer design of Tamara Floyd. Tamara graciously allowed me to test some of her devices well before I had an appreciation for how much work went into making them. The result is that I broke almost all of them. In the end, I had a packaging scheme that worked and saved me from breaking all of my own reactors down the road. The collaboration with her, as seen in the first chapter, resulted in an understanding of mixing and reaction at the micro scale which had a direct impact on the design for the gas-liquid contacting scheme.

The work with the phosgene chemistry in chapter 4 is a result of a collaboration with Sameer Ajmera. The details of the analysis are left to him, but I think the work provides a reference point for what really is a 'fast reaction.' It provides a contrast for the multiphase hydrogenation reaction, and as a result, provides further insight into microreactor design. Perhaps the greatest accomplishment is that we lived to see the data. But I do appreciate his patience and it was overall an enjoyable experience.

It was a real pleasure to be able to work with Shinji Isogai of Mitsubishi Chemicals. His work with multiphase oxidation reactions with these microreactors was a particularly good example of the benefits of process intensification. Shinji's work ethic would put any graduate student's to shame (particularly this one's) and his polite and accommodating personality were appreciated by everyone in the lab.

A good portion of the gas-liquid contacting study in the microstructured reactor was performed by Sonia Tulyani, an undergraduate who stuck with the project for the course of her undergraduate research. She is not only a student of incredible patience and skill, but she also was wonderful to work with. MIT needs more undergraduates like her.

Chapter 6 describes the incorporation of porous silicon into the microreactors. Porous silicon studies were initiated by David Quiram and continued by Rebecca Jackman. Rebecca and I collaborated for the porous silicon integration in this thesis. If there was ever a process that was truly 'black magic,' this was it.

Other people in the group have contributed throughout with both major and minor details. Aleks Franz and Samara Firebaugh both provided insight and guidance throughout the device and fabrication designs.
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1. Introduction

1.1. Motivation and Thesis Overview

The ability to carry out chemical reactions at a large scale with high yield, absolute process control, and with economic efficiency is at the core of chemical engineering. The modern chemical plant contains a whole host of operations which serve to transform materials, in a controlled and efficient fashion, from one form to another. Understanding chemical processes requires tools that can probe reaction kinetics efficiently and accurately, and this too, is a critical component of chemical engineering. In the evolution of technology, more advanced methods for reactor construction and chemical analysis are increasingly becoming available. New technologies are developed in seemingly unrelated fields and eventually these technologies diffuse out and find diverse and varied applications. This thesis is about such technology application in the area of reactor design and reaction engineering.

The technology in question is microfabrication. The development of modern integrated circuits has produced manufacturing processes that deposit thin layers of materials ranging from glasses to metals, carve out features in these materials smaller than a micron, and all of it is done in replicate across large areas. The modern Pentium processor has nearly 10 million individual transistors in an area of 4 cm²: each transistor is a fraction of a micron in size (for reference the human hair has an average diameter of about 50 microns). Multiple layers of metals and glasses cover and connect to the transistors to create the microelectronic circuit.

Coinciding with this microelectronics revolution has been the development of mechanical instruments at this microscopic scale using much of the same technology.
When coupled with electrostatic forces for manipulating and sensing the mechanical instruments, the collective term to describe the technology is micro-electro-mechanical systems (MEMS). Today's research in MEMS covers a broad array of future applications. Ranging from the fanciful micromachines that could one day travel throughout the body to report or repair on damaged tissues to miniature aerial vehicles, MEMS is a field of great imagination and prospect. The reality for MEMS today is no less impressive. The most widespread application is the miniature pressure sensor which is used in a number of systems in the modern automobile. These MEMS devices measure the deformation of a thin membrane and transduce the mechanical pressure to an electrical signal. The miniature accelerometer for air-bag deployment in an automobile is another example. The digital mirror display (DMD) made by Texas Instruments is a MEMS device consisting of arrays of microscopic mirrors. Electrostatic forces cause each individual mirror to deflect hundreds of times per second, to reflect an incident light beam upon or away from a target. In this way, a continuous moving image is projected with super digital clarity and fidelity. The inkjet printer is another widespread MEMS application: a miniature nozzle, coupled with the microelectric generation of bubbles, forces ink as a steady stream of droplets on to the paper.

The technology that unites these varied MEMS applications is silicon microfabrication. Starting with substrates of pure single crystalline silicon, thin films are deposited, photolithography is used to pattern arrays of small features, plasmas or acids are used to selectively etch the films or silicon, and multiple substrates are bonded together to produce the mechanical and electrical elements of a single chip. The chip is
packaged within a larger system of components to create a functional sensor, instrument or device.

The motivation for applying this technology to chemical processing is a result of a number of enabling features of the microfabrication process. First of which, the ability to create small features with large aspect ratios is an ability unique to microfabrication. Conventional machining is limited to features 100 μm in size and the depth is limited to the same. Furthermore, conventional machining is serial in nature, requiring lots of time for complex geometries. Silicon micromachining, particularly deep reactive ion etching, allows features much smaller to be created simultaneously. For example, the inlet channels of the single channel reactor of chapter 2 are only 25 μm wide and nearly 300 μm deep. What advantage do small channels have for chemical processing? As the size of the channel decreases, the relative ratio of channel surface area to channel volume increases. This increased surface area has a direct impact on thermal and mass transport. The ability to keep a reactor at a constant temperature, even in the presence of a highly exothermic reaction, is improved as the surface area for heat conduction increases. Similarly for mass transport, as the length scale for diffusion is reduced, the time to reach homogeneous fluid mixtures is reduced. This advantage is discussed in more detail throughout this thesis with the primary objective to demonstrate quantitatively the improvements in heat and mass transfer for chemical reactions in microsystem. In addition to constructing small features in replicate, silicon microfabrication has a host of additional features, including the ability to construct thin film sensors and electronics. This allows for the direct integration of functionality with the reactor, such as temperature measurement, heating, pressure measurement, and specific chemical
identification and detection. Figure 1-1 is a photograph of the microreactor device that is
the culmination of this thesis. It is a chip (1.5cm X 4cm) consisting of 2 layers of silicon,
2 layers of glass, 10 parallel reaction channels filled with 20,000, 50μm diameter catalyst
supports, a platinum thin film element for heating and platinum thin film resistor for
temperature measurement. The rest of this thesis will describe the design, fabrication and
characterization of this device as well as the devices which led up to its design.

The next section of this chapter provides some of the background work in the area
of microreaction systems prior to and during this thesis. It covers a range of applications
proposed and demonstrated for microchemical systems and lends further motivation to
this area of research. In addition, providing a short survey of other efforts in
microreaction research goes toward showing the novelty of the present work. Following
this background is a section describing multiphase reactions and the most common
reactor designs found in industrial applications. The limitations of these industrial
reactors lends motivation towards the research of this thesis which focuses upon novel
reactor designs for multiphase processes. This chapter finishes with an outline for the
rest of the thesis.
Figure 1-1. Microstructured microreactor chip. Ten channels (625μm X 300μm X 20mm) are connected in parallel. Four segments of a thin-film platinum heater overlap the channels. Photograph courtesy of Felice Frankel.
1.2. **Background on Microreaction Technology**

The last decade has seen an explosive growth in research and development in the miniaturization of chemical processes.[1] [2] Benson was one of the first to propose that miniaturized chemical systems could provide modular, distributed production units thereby allowing a manufacturing process which was more flexible to market forces, portable, safer for the generation of hazardous chemicals, and more efficient by virtue of improved heat and mass transfer.[3] Since then, a multitude of technologies have been developed and applied for the purposes of creating miniaturized chemical unit operations, including both silicon microfabrication[4] and conventional machining of metals[5]. An international conference on microreaction technology, started in 1996 and continuing today, illustrates the wide-spread interest that has been generated.[6, 7] The potential for chemical synthesis in a microsystem has been addressed by several authors.[8-14] This interest in micro chemical synthesis is in addition to a larger body of work devoted to the miniaturization of analytical chemistries, Micro Total Analysis Systems (μTAS).[15-18]

The premise for using a miniaturized device for chemical synthesis is that production scale quantities are achieved as a result of numbering up, or operating a number of devices in parallel, rather than redefining the scale of the device itself.[19] This is a radical departure from traditional modes of chemical processing which involve a few, very large chemical plants. The motivation for operating a multitude of reactors can stem from several factors including an enhanced unit productivity (owing to higher heat and mass transfer), better control, and safer operation. Part of the reason why this mode of operation has yet to be explored is that the control systems required to manage such a complex network of operations has only recently become available with the advent of

23
modern computing. The overriding assumption in this thesis, when analyzing the microreaction devices in the context of chemical synthesis, is that numbering-up or parallel synthesis is a viable route to scaling up a process. The motivation for this study is to elucidate those chemical processes which could be suitable for parallel synthesis and to demonstrate a microreaction unit with sufficiently superior performance that process intensification is justified.

In addition to chemical synthesis, microreaction systems have the potential to improve the investigation of chemical processes. One way is to improve the efficiency of experimentation by increasing the through-put of data collection and analysis. The high-throughput screening of catalysts is such an example and has received considerable attention recently.[20-23] Another way is to eliminate the effects of heat and mass transfer in disguising the true kinetics of a fast exothermic chemical reaction. Yet a third benefit is the ability to work with small volumes of reagents. For a pharmaceutical intermediate, the reagent can be in short-supply, or for a toxic chemistry the small volumes can make the investigation safer.

It is the ability to define microscopic geometries with high surface area to volume ratios which makes microreactors attractive to a host of chemical processes. Multiphase processes specifically, could benefit because mass transport across phase boundaries is often the limiting step in a reactive process. On an industrial scale, multi-phase reactors have a wide variety of designs. The choice of design depends on several variables, including the scale of the operation, the nature of the catalysts involved, and the severity of mass transfer limitations.
1.3 Background on Multiphase Chemical Processes

Many of today's chemical reaction processes involve multiple phases, and the value of chemical products generated by multiphase reactor technology has been estimated at over $600 billion annually.[24] Most multiphase processes are those involving the reaction between a gas phase and a liquid phase. The reaction between two immiscible liquids, or a solid reacting with a gas or liquid could also be considered multiphase, but occur less frequently. The reasons for having to react a gas and liquid phase vary. In the case of petro-chemicals or specialty chemicals, the costs associated with heating the liquid to the gas phase may be too high, especially if the reaction is carried out at elevated pressures or the hydrocarbon has limited volatility. For pharmaceuticals, the liquid reactant of interest may decompose before it volatilizes. Reactions between gases and liquids are ubiquitous throughout chemical processes ranging from absorption processes (scrubbing CO₂ into amine solutions) to reactive (chlorination of aromatics). The reactions can either be homogeneously catalyzed, as in the case of chlorinations where the catalyst is a Lewis acid such as FeCl₃ dissolved in the substrate, or heterogeneously catalyzed, such as catalytic hydrogenations using noble metals dispersed on inert porous materials.

The reactors available for carrying out these gas-liquid reactions vary from co-current and countercurrent bubble column reactors to highly agitated slurry batch reactors.[25] The principle consideration in all cases though, is the rate of transport of the gaseous reactant into the liquid. It is this transport process which may ultimately limit the rate of conversion as opposed to the intrinsic kinetics of the chemical reaction itself. Affecting this rate of transport has been the subject of immense study.
Examples of some of the more common reactor configurations for multiphase chemical processing are listed in Figures 1-2 and 1-3. Figure 1-2 presents the reactor options for processes in which most of the reactor volume is occupied by the liquid phase, while Figure 1-3 presents the reactor options when a solid packing material is contained within the volume. The choice of reactor for a particular operation depends upon a number of factors, including the scale of the operation, the relative rates of gas absorption to reaction and the nature of the catalyst involved. For small volume operations, such as those found in most pharmaceutical manufacturing processes, the predominant reactor

![Bubble Column Reactor and Slurry/Agitated Vessel](image)

**Figure 1-2.** Common gas-liquid reactor designs. Both the bubble column and the slurry reactor are comprised primarily of the liquid phase.
choice is the agitated vessel or slurry reactor. However, continuous reactors have several advantages for miniaturization, as will be discussed in the next chapter.

Continuous industrial multiphase reactors are usually classified according to their flow dynamics. In trickle bed reactors, for example, the volume of the reactor is predominantly the gas phase and the liquid forms a thin film around the catalyst pellet. This contrasts with the bubble column reactor, where the predominant phase is liquid and the gas is dispersed as bubbles throughout the volume, or the packed bubble column reactor.

Figure 1-3. Common multiphase packed-bed reactor designs. The trickle-bed reactor is primarily filled with the gas phase, but flow can either be co-current or countercurrent with gas flow either upward or downward.

reactor where the predominant phase within the reactor is the liquid phase. A wide range of variations on these designs exist, all intended to better promote the mixing between the
gas and liquid phases. The designs for the bubble column reactors aim to produce large packets or trains of small diameter bubbles; preventing the coalescence of the gas is tantamount to maintaining a high interfacial area between the two phases. It is this interfacial area which determines the rate of transport into the liquid phase for a given flux. For this reason, the reactor is designed to maximize the interfacial area. The jet-loop reactor, for instance, is an extreme example of achieving high-levels of gas-liquid dispersion and mass transfer. The high velocities produced come at the expense of high power consumption, but the mass transfer is the highest of the various reactor types.

The packed column reactors are either filled with an inert material or filled with a catalyst which plays an active role in the reaction process. The heterogeneous reaction requires that both the liquid phase and the gas phase reactant adsorb onto the surface of the active catalyst. The active catalyst is usually contained within the pores of an inert, high surface area material and so there is an additional opportunity for transport limitations within the pores of the catalytic material. Mass transfer limitations become compounded as transport of the gaseous reactant is hindered by its adsorption into the liquid, its diffusion and transport with the liquid to the catalyst, and then finally within the pores of the catalyst itself. Because of the multitude of mass transfer resistances, these three-phase, gas-liquid-solid reactions present the greatest opportunity for making improvements in mass transfer through engineering at the micro-scale. The microreactors presented in this thesis involve heterogeneously catalyzed gas-liquid reactions and their behavior more closely resembles that of the three-phase packed-column, or trickle-bed reactors.
1.3.1 Trickle-Bed Reactors

Trickle-bed reactors have generally found application in large scale petrochemical processing and there has been a large body of knowledge collected over the last several decades. [27-31] The reactor consists of a column ranging in diameter from 5 cm (laboratory scale) to several meters (industrial scale) filled with catalyst pellets or cylinders ranging in size from 4-10mm in diameter. The gas and liquid phases can flow either co-currently or counter-currently, but the liquid flow is down through the packing. The flow relies upon gravity to pull the liquid downward and relies upon capillary action to distribute the liquid through the porous solids pellets. Because of the relative volume fractions of the phases, the liquid 'trickles' through the packed-bed.

Challenges in designing trickle bed reactors include reducing pressure drop, achieving a uniform distribution of the fluids within the reactor, and reducing internal and external hindrances to mass transport. Figure 1-4 depicts the ideal configuration of the phases for a catalyst particle in a trickle-bed reactor. The liquid forms a thin film over the catalyst through which the gas must diffuse in order to react at the solid surface. Deviations from this ideal configuration include partial wetting of the catalyst particle, partial drying of the catalyst particle (where some volume of the catalyst contains only the gas phase) or increases in the thickness of the liquid layer due to macro scale flow distribution. This variation from ideal conditions is characterized as the 'wetting efficiency' of the trickle bed and can impede performance in addition to all the other mass transfer resistances.
Uneven flows can lead to incomplete utilization or local zones of varying reaction rate and heat transfer. Poor distribution of the fluids can thus lead to local ‘hot spots’ which can decrease the selectivity of the process, reduce catalyst life, or lead to side reactions which may cause reactor runaway.[32] Poor thermal management can also decrease the life of a catalyst (temperature excursions can sinter the metal of the catalyst and reduce the active surface area) and further reduce the efficiency of a reactor. Temperature control can be critical, especially when the reaction involves a flammable and explosive gas such as hydrogen, the most common gas-phase reactant for gas-liquid-solid reactions.
1.3.2 Hydrogenation Reactions

The most common chemistry for gas-liquid-solid reactors is the heterogeneously catalyzed hydrogenation reaction. Hydrogenation reactions span all scales of chemical production, from pharmaceuticals to commodity chemicals. Numerous examples abound. Within petrochemicals at the large scale, hydrogenation is used to convert malic anhydride to 1,4-butanediol. In 1994, 300,000 metric tons of 1,4-butanediol was produced, primarily as the feedstock for making tetrahydrofuran (THF), a common industrial solvent. [33] Within pharmaceutical and fine chemicals, nearly 20% of all synthetic steps are catalytic hydrogenation.[34] For example, the hydrogenation of glucose to sorbitol is used in the synthesis of vitamin C; 30% of the steps in the manufacture of Vitamin E are catalytic hydrogenations. Another example is the catalytic hydrogenation of p-isobutylacetophenone, an intermediate in the process for ibuprofen. The hydrogenation of nitro compounds finds use in the hydrogenation of 2,4-dinitrotoluene to toluenediamine. Toluenediamine is reacted with phosgene (chapter 2) to produce toluenediisocyanate(TDI), another important industrial solvent.

As a class of reactions, hydrogenations pose several challenges. Hydrogenations are relatively exothermic (100-400kJ/mol), so temperature control and thermal uniformity can be important issues. Hydrogen has a low solubility in most liquids causing the reactions to be limited by the concentration of hydrogen even for low concentrations of the liquid reactant (the solubility of hydrogen in an organic solvent is near 4×10⁻⁶ mol/cm³, while the liquid concentration is ~ 1×10⁻³ mol/cm³). As a result of this low solubility, many hydrogenation reactions are operated at elevated pressures to increase
the solubility (often as high as 100 atm). The elevated pressures exacerbates the explosion hazard of the hydrogen gas and complicates the equipment design for the reactor.

**Range of Reaction Rates**

Independent of temperature and pressure, hydrogenations can have wide range of reaction rates. A useful measure of comparison is the turn-over-frequency, which is the reaction rate per active catalyst site (mols converted / mols catalyst / time). Table 1-1 compares the relative rates for various hydrogenation rates at room temperature and atmospheric pressure (for some of the reactions, the value has been calculated to ambient conditions).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>TOF (s⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Citral Hydrogenation</td>
<td>0.2</td>
<td>[34]</td>
</tr>
<tr>
<td>Cyclohexene Hydrogenation</td>
<td>8</td>
<td>[35]</td>
</tr>
<tr>
<td>Itaconic Acid</td>
<td>200</td>
<td>[36]</td>
</tr>
<tr>
<td>Soyabean Oil</td>
<td>0.1</td>
<td>[36]</td>
</tr>
<tr>
<td>Soyabean Oil(160C, 4atm)</td>
<td>120</td>
<td>[36]</td>
</tr>
<tr>
<td>Ethyl Pyruvate</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

The liquid phase hydrogenation of citral, a compound simulating a host of pharmaceutical intermediates, exhibited a turn-over-frequency of 0.2 s⁻¹ using a 1wt% Pt/SiO₂ catalyst.[37] In a study using 5 wt.% palladium supported on carbon, the reaction rates for the hydrogenation of soyabean oil and itaconic acid (HO₂CCH₂C(=CH₂)-CO₂H) were investigated.[36] The hydrogenation of vegetable oils
is a prevalent example of large-scale hydrogenation reactions and soyabean oil is a representative triglyceride. Triglycerides require partial hydrogenation for the manufacture of edible oils because the unsaturated oils (containing carbon-carbon double bonds) are subject to oxidation resulting in short shelf-lives. At room temperature the rate of reaction for the triglyceride hydrogenation is relatively slow (TOF calculated to be 0.1 s\(^{-1}\)). For this reason, the reactions are run at elevated temperatures and pressures where the reaction rates are considerably faster. At these elevated conditions, the reactions are reported to be limited entirely by the diffusion, or mass transfer, of hydrogen.[36] The hydrogenation of cyclohexene, the model reaction performed in this study, is moderately fast with a TOF = 8 s\(^{-1}\).

1.3.3 Previous Micro Trickle-Beds

The construction of a 'micro' trickle bed reactor has been illustrated by Germain et al. for precisely the reason of eliminating mass transfer limitations.[38] The particle size of the catalyst was in the range of 100-200 \(\mu\)m and the reaction investigated was the catalytic hydrogenation of glucose to sorbitol. Although few details have been published, this is the only example of a reactor employing catalyst particle sizes smaller than a millimeter.

A cross-flow sandwich structure has been investigated for improving gas-liquid mass transfer. The reactor design was found to have better mass transfer performance relative to a conventional packed bed, although specific mass transfer coefficients were not provided.[39] This provides another example of the extremes to which reactors will be designed in order to alleviate mass transfer limitations.
1.4 Motivation for Microscale Multiphase Chemical Processes

Multiphase reactions present a unique opportunity for microfabricated reactors.\cite{14} In addition to efficient thermal control, these systems have the added complexity of forcing a reactant of one phase to mix, diffuse, and react with that of another. For fast gas-liquid-solid reactions, the chemical kinetics are often limited by the mass transfer rate of the gaseous species through the liquid to the surface of the catalyst. As a class of reactions, hydrogenations represent a typical and ubiquitous gas-liquid-solid reaction. Hydrogen is reacted with an organic substrate over a supported noble metal catalyst in either a slurry reactor or in a packed bed arrangement. The limited solubility of hydrogen in organic substrates and solvents makes mass transfer a primary concern.\cite{26} Consequently reactions are often operated at high pressures, sometimes as high as 100 atmospheres\cite{30} to increase the reaction rate and offset the low hydrogen solubility. However, in that case the explosion potential requires extreme safety measures.

The opportunity for microreaction systems to impact multiphase reactions has been recognized by other investigators.\cite{40-45} The novelty of the present work is 1) the presence of the heterogeneous catalyst (which provides another opportunity for improving mass transfer), 2) the use of silicon micromachining and the integration of sensor functionality, and 3) the engineering of microstructural features within the reaction channels to manipulate gas-liquid flow and increase the interfacial gas-liquid contact area.
1.5 Thesis Objectives

The objectives of this thesis are to investigate novel chemical reactor designs for multiphase reactions which are enabled by microfabrication methods. Multiphase reactions which specifically focus on reactions between gas and liquid phases are emphasized because the gas-liquid interface presents a resistance to mass transfer. This resistance can be mitigated by engineering at the micro scale by reducing the length of diffusion and increasing the total contact area of the interface. One goal is to demonstrate improved mass transfer such that improved overall reaction rates can motivate the use of microreactor systems for chemical synthesis. Another goal is to study the behavior of two-phase flows in microfluidic devices to provide a greater understanding of the engineering of microdevices for multiphase applications. Yet a third goal is to create entirely novel reactor designs which have not previously been considered in the chemical engineering literature because the fabrication technology (silicon microfabrication) has not been available.

1.6 Thesis Outline

Having outlined the relevant previous work on microfabricated chemical reactors, particularly those for multiphase gas-liquid reactions, the rest of this work will focus on a number of devices for multiphase systems, their design, fabrication, and characterization. Chapter 2 begins with a study of mixing liquids in a microchannel device. The results of that study provide the backdrop and motivation for the design of the first single channel multiphase reactor. As a demonstration of the ability to incorporate catalysts and carry out hazardous reactions in a controlled fashion, the gas-phase synthesis of phosgene is
conducted in this single channel reactor. Within chapter 2, the experimental methods for most of the thesis are described, including the packaging of the reactor chip and the physical set up for the experiments. Chapter 3 presents the design and fabrication of the 10 parallel channel, or multi-channel reactor, which is a logical extension of the results from chapter 2. In addition, several features are added, including thin film resistors for heating and temperature control. Chapter 3 contains much of the thermal characterization for the devices. After describing the design of the two principal devices, chapter 4 details the experimental results for the catalytic gas-liquid hydrogenation of cyclohexene. Pressure drop, multiphase fluid dynamics, and reaction rate results are described. Using this model reaction, the mass transfer for gas-liquid absorption is characterized in chapter 5. The final reactor design presented in chapter 6 is that of the microstructured or integrated catalyst reactor. This device, more so than the previous two, is an original design enabled by microfabrication. Chapter 7 provides the results for gas-liquid two-phase flow phenomena in these microstructured reactors. Chapter 8 summarizes the results for the reactors of this thesis and provides a comparison with industrial reactors. Chapter 9 finishes the thesis with conclusions and opportunities for further study.
2. "Single-channel" Reactor Design and Applications

2.1. From Gas-Phase to Liquid Phase: Background for the first design

The gas phase membrane microreactor depicted in Figure 2-1, designed and tested by Ravi Srinivasan throughout 1995-1997, is one of the first MEMS microreaction devices ever constructed. [46] Designed to carry out high temperature gas-phase reactions, it consists of a membrane heated with thin-film platinum resistors, a thin platinum film as

![Membrane microreactor illustration](image)

**Figure 2-1.** Membrane microreactor illustrating the integration of multiple thin film heaters and resistive temperature sensors onto a chip for the gas-phase partial oxidation of ammonia. Courtesy R. Srinivasan.
catalyst, and a ‘T’ geometry for mixing two reagents on chip. Two issues are of paramount importance for its influence on the design of subsequent microreactors: the nature of the catalyst and the nature of the on-chip mixing. The issue of the catalyst design will be revisited later in section 2-3. The issue of mixing is treated here briefly, because it is represents the principal design feature required for reactors involving condensed phases.

In order for any chemical reaction to occur between two different reagents, they first have to mix, and if needed, be transported to a catalytic surface. For gases, the process of mixing is fast, owing to their large binary diffusivities (D = 1-10×10^-5 m^2/s). For the channel dimensions in the gas-phase microreactor (500 μm), the characteristic time for diffusion (τD=L^2/D) is 25 milliseconds. Furthermore, Reynolds numbers are low so that the flow is laminar and mixing occurs without the aid of turbulent convection. According to Srinivisan,[47] the rate of the reaction and the required residence time is such that the gas phase is a homogeneous mixture once the flow reaches the catalytic portion of the reactor. Hence a simple geometry such as a mixing ‘T’ is sufficient to react two gas-phase reagents.

The case for liquids is more complex. Binary diffusivities are much lower (D = 1-10×10^-9 m^2/s). As a result, if two liquid reagents were to be mixed in the above reactor geometry, several minutes would be required before the two liquids could be considered a homogeneous mixture. The reaction would be hindered by the inability for the two reagents to successfully transport in equal concentrations to the catalytic surface. Usually one can depend upon turbulence to achieve rapid mixing in a continuous flow reactor. However, at these small channel dimensions, turbulence is difficult to achieve. To
address this micromixing problem, several strategies have emerged based on short diffusion lengths and numerous studies have been performed on mixing liquid reagents in microfabricated devices.[48-52] The goal is to reduce diffusional lengths and generally this is done by splitting up and interleaving the inlet streams. Another strategy, with an added level of fabrication complexity, makes use of chaotic advection.[53, 54] The utility of this latter approach is unclear, as the devices are complicated in construction.

Most of the micro-mixer designs, in one form or another, take advantage of the dependence of the diffusional mixing time upon the square of the characteristic length. The streams to be mixed are contacted in such a way that the contact area between the streams is large and the width of the streams is small. Since the diffusion time scales with the square of the length, mixing times can be quite rapid when the length for the diffusion is on the order of microns.

Using the liquid phase microreactor designed and fabricated by T. Floyd[48], mixing characterization was performed and the principle of multilaminar mixing was studied. Liquid-phase mixing studies were performed as part of this thesis in order to understand mixing strategies before designing devices for more complicated multi-phase flows. Figure 2-2 is a top-view of the microreactor, showing how the fluids enter radially aligned inlet ports and flow through the device. The liquid-phase microreactor achieves rapid mixing of the reagents by dividing the reagents into multiple laminar streams and then contacting the streams such that the contacting area is maximized. The two reagents to be reacted are first split into five laminar streams each. These streams are contacted and then focused into a narrow (50 μm) channel. By focusing these laminar
streams into a narrower channel, the length scale for diffusion is shortened even more. The channels are etched into a silicon layer and a glass layer caps the channels from the top. Fluids enter the device from ports underneath the device located at the ends of each of the streams.

**Figure 2-2.** Liquid micromixer design. Two sets of radially aligned inlets split and interleave two mixing liquid reagents. The streams are then focused to a narrow 50 μm wide channel for reaction and analysis.
**Figure 2-3.** Experimental visualization of an acid-base reaction in the liquid-phase micromixer. Red streams contain phenol red pH indicator at pH 8 (red), yellow streams contain 0.1M HCl. The diffusion of the acid into adjacent streams is dictated by the flow rates.

A) Liquid flow rate = 0.05mL/min.
B) Liquid flow rate = 0.2 mL/min.

This method extends the concept of mixing by lamination by contacting 10 laminar streams in a single pass.[55] Moreover, the high aspect ratio of the channels allows for higher throughput of reactants, which is desirable for chemical synthesis. As a
qualitative assessment of mixing versus flow in the device consider figures 2-3A and 2-3B. A pH indicator, phenol red, is mixed with an acid at a low flow rate (0.05mL/min). As the acid diffuses into the adjacent stream, the pH drops below the color transition point of the indicator and the color changes from red to yellow. By increasing the flow rate, and hence reducing the time that acid has to diffuse into the adjacent streams at a given point, the extension of the red (unmixed portion) streams is increased.

As a more quantitative assessment, acid-base reactions, coupled with fiber optics and UV-visible spectroscopy were used. Monitoring the absorbance of a pH indicator with an acid base reaction is a commonly used method for assessing the mixing behavior. Since the acid-base reaction is fast, the kinetics, as measured through the absorbance of the pH indicator, is controlled by the mixing of the reagents. Figure 2-4 is an experimental visualization of laminated mixing streams. Phenol red indicator in phosphate buffer solutions at pH = 6.8 and pH = 8.0 produce the yellow and red streams respectively. At a discrete point down the length of the reactor, the absorbance is measured as a function of flow rate. Figure 2-5 is a UV-VIS spectra of the two buffer solutions fed independently to the reactor, as well as the spectra for the mixing of the two reagents at equal flow rates. Because the signal collected is averaged over the entire width of the channel, a reaction is necessary to assess mixing. Simply using a dye in one of the streams would be insufficient because the average concentration would be the same before and after mixing. For these experiments, both streams contain the same concentration of the phenol red indicator; it is the diffusion of the acid which causes the color change. Figure 2-6 shows the decay of the absorbance for the red indicator as a function of the contact time.
Figure 2-4. Experimental visualization of laminar flow with two reagents for UV-Vis mixing characterization (buffered phenol red pH 8.0 and 6.8).

Figure 2-5. UV-VIS spectra collected in the microreactor. The pH 8.0 reagent has an absorbance maximum at 560 nm. When mixed with the pH 6.4 reagent, the absorbance at 560 nm decays due to the acid base reaction and the transition of the color pH indicator. In this way, the mixing is quantitatively assessed.
The contact time here is defined as

\[ \tau_{\text{contact}} = \frac{L \cdot A_s}{Q} \]

where \( Q \) is the volumetric flow rate, \( A_s \) is the cross-sectional area of the channel and \( L \) is the length down the channel at which the absorbance is collected. As the flow rate is decreased, the time at which two adjacent streams have been allowed to contact and mix is increased. The absorbance decays as a result of the acid-base reaction, which is a result of the mixing. The extent of mixing is a parameter than can be defined to assess the relative degree of mixing, since complete mixing, in the mathematical sense, would only occur for a flow rate of zero. The absorbance of a solution premixed with both reagents in equal amounts is defined as 100% mixed. The absorbance of the red reagent flowing through the reactor in the absence of reaction is defined as 0% mixed. The measured absorbance is used to calculate the extent of mixing based on this linear scale. Using the data cited above, the acid-base reagents are 90% mixed for a contact time of 10 milliseconds in the microreactor. This compares favorably to the characteristic diffusion time of 6 milliseconds (assuming \( L = 2.5 \mu m, 1 \times 10^{-9} \text{ m}^2/\text{s} \)).

The conclusions resulting from this study of diffusion and reaction in continuous flow microreactors influenced the choice of design for the multiphase reactors in a number of ways. First, since flow is entirely laminar, the method of splitting reagents into multiple laminar streams and interleaving them to reduce diffusional lengths is a successful strategy at the micro scale. Second, from a fabrication standpoint, deep reactive ion etching allows high aspect ratio channels which can produce deep, narrow streams for optimal contacting. The fabrication layout for the multiphase reactors is an
extension of the liquid microreactor fabrication: deep etching channels in silicon and
capping them with a layer of glass.

![Graph showing absorbance decay over contact time](image)

**Figure 2-6.** Absorbance decay as a result of mixing. The absorbance peak at 563nm is tracked versus flow rate and position along the microreactor. As the extent of mixing increases with increased contact time, the absorbance decreases to a steady mixed value (see Figure 2-5). Error bars represent one standard deviation with 3 samples per data point.
2.2. Single channel reactor design

The design of the single channel reactor was influenced by two principal considerations: the capabilities of existing fabrication processes and the nature of the chemistry. For heterogeneously catalyzed reactions, the high surface areas of traditional porous supports allow for a greater dispersion of the active surface sites and consequently, a higher reaction rate per volume of support. For reactions of moderate rate, such as some hydrogenations, processing in small volumes demands the highest attainable active surface area in order to have a practical reactor throughput. Planar metal films, while easy to integrate using thin film methods, can not attain the same active area through geometry alone. So while thin film catalysts are sufficient for fast gas-phase reactions such as ammonia oxidation, higher surface area catalysts can extend the range of applicable reactions in the microenvironment. For the planar platinum film of the gas-phase reactor with dimensions of 500μm × 1cm, the active surface area is on the order of 0.5cm², not accounting for surface roughness which would increase this value slightly. In a 3-D configuration of porous catalyst particles (1wt% platinum supported on a porous alumina) with active surface area of 0.6 m²/g, the metal surface area is 30X larger at 15 cm² (assuming the same geometry with a height of 500μm and a packing density of 1 g/cm³). The surface area of metal available for reaction is higher with the porous particles even though there is more metal by weight with the thin film deposition.

The advantage of using standard catalysts, such as noble metals supported on inert porous materials is the readily available information on chemical kinetics. Catalyst preparation becomes a matter of separating discrete particle size ranges and loading the reaction channels. Common methods for fractioning powders into particle size ranges
using sieves exist and can separate particles as small as 30 μm. Uniformly sized polystyrene particles sized 1-5 μm are routinely used in column packings for chromatography applications.

Available photolithography methods enable features as small as 1 micron, so in theory, a filter structure could be built to allow the packing of particles this small. The first design feature in order to accommodate micron size particles is to create such a filter structure for capturing particles and retaining them within the device while allowing reactants to flow continuously through the packed bed. Several designs are available for microfabricated filters. [56-58] The method employed here was to create an array of columns fabricated simultaneously with the main reaction channels. Figure 2-7 illustrates the design choices for a microfabricated filter, accounting for the etch variation associated with different sized features. Depending upon the specific etch process, features with a smaller critical dimension etch slower than larger features due to diffusional limitations of the gas-phase products. The greater the disparity in feature sizes (such as that between the 625-μm-wide reaction channel and the 25-μm-wide filter) the greater the difference in etch depths. The critical issue in choosing the appropriate size for the packing material is the pressure drop.
Figure 2-7. Design options for microfabricated filter structure. Smaller gaps (bottom) necessitate shorter etch depths and a greater disparity in depth between the filter unit and the reaction channel.

For microreaction systems in general, the engineering design challenge is to balance the gains made in heat and mass transfer against the losses in pressure drop. The pressure drop for a packed bed of spherical particles can be estimated from the Ergun equation,

\[
\frac{\Delta P}{L} = \frac{G}{\rho D_p} \frac{(1-\varepsilon)}{\varepsilon^3} \left[ \frac{150(1-\varepsilon)\mu}{D_p} + 1.75G \right] \tag{2-1}
\]
or

\[
\frac{\Delta P}{L} = \frac{150 \cdot G \mu (1 - \varepsilon)^2}{D_p^2 \rho \varepsilon^3} + 1.75 \frac{G^2}{\rho D_p} \frac{(1 - \varepsilon)}{\varepsilon^3}
\]

(2-2)

where \( G \) is the superficial mass velocity, \( \varepsilon \) is the void fraction, \( D_p \) is the particle diameter, \( \mu \) is the viscosity and \( L \) is the length of the packed bed.[59] For the relatively small velocities in this work, the second term is negligible. Substituting \( G \) with the volumetric flow rate \( Q \), the cross-sectional area of the reactor, \( A_s \), and the density, gives the following functional dependence:

\[
\frac{\Delta P}{L} \propto \frac{\mu \cdot Q}{d_p^2 \cdot A_s} \frac{(1 - \varepsilon)^2}{\varepsilon^3}
\]

(2-3)

As an example, for a flow rate of 0.5 mL/min, and the cross-sectional area of the reactor (width=625\(\mu\)m, depth =300\(\mu\)m), the superficial velocity is \( U = 4.44 \text{ cm/s} \).

Using the following values in the Ergun equation (2-1), \( \varepsilon = 0.4, \mu = 0.012 \text{ g/(cm s)}, D_p = 64 \mu \text{m}, \) and \( \rho = 0.8 \text{ g/cm}^3 \), gives \( \Delta P/L = 0.11 \text{ MPa/cm} \).

Table 2-1 contains the calculated pressure drops for various sized particles. The channel geometries are the same as above with a bed length of 2 cm and a flow rate of 0.1 mL/min.
Table 2-1. Calculated Pressure drops for based on Erguns equation.

<table>
<thead>
<tr>
<th>Particle Diameter</th>
<th>Pressure Drop</th>
</tr>
</thead>
<tbody>
<tr>
<td>64 μm</td>
<td>0.044 MPa</td>
</tr>
<tr>
<td>5 μm</td>
<td>7.2 MPa</td>
</tr>
<tr>
<td>1 μm</td>
<td>180 MPa</td>
</tr>
</tbody>
</table>

What becomes apparent is that for particles smaller than 10 μm, the calculated pressure drops are beyond practical feasibility. Particles, 5 μm in diameter, in this geometrical arrangement would have a pressure drop of 7.2 MPa or nearly 1000 PSI! As will be shown later, the actual flow rates required for an appreciable rate of conversion is slightly reduced at 0.01 mL/min. This would reduce the pressured drop by a factor of 10, but even so, the pressure drop would become unmanageable. Later in this chapter, experimental values for the pressure drop are measured in a microchannel and the Ergun equation is shown to apply, even at this reduced scale.

Consequently, the pressure drop sets the lower limit of particle sizes for a given geometrical configuration and flow conditions. The upper limit for particle sizes is set by the need to eliminate channeling and flow maldistributions at the walls of the packed bed. As the particle size approaches some fraction of the channel diameter, void spaces become uneven at the walls causing flow to channel near the walls rather than through the packed-bed. Although, there is no universal rule for defining the ratio of channel diameter to particle size, a value of at least 6-10 is often used. [60] Therefore, for a channel height of 300 μm, a particle size of 50 μm would be at the upper limit for a ratio of 6.
Having determined that the optimal particle diameters for pressure drop would be in the range of 50 microns, the filter structure designed included columns 40 \( \mu \text{m} \) wide with a spacing of 25 \( \mu \text{m} \). Figure 2-8 depicts the exit portion of the channel along with a scanning electron micrograph of a cross-section of the reaction channel with the filter unit. The etch non uniformity of the process can be seen as the depth in the 25 \( \mu \text{m} \) gaps is not the same as the main reaction channel (625 \( \mu \text{m} \)).

Figure 2-9A illustrates the inlet portion of the reactor. Gas and liquid inlet flows are split among several 25-\( \mu \text{m} \)-wide channels which meet at the main reaction chamber which is 625 \( \mu \text{m} \) wide. Perpendicular to these inlet channels are two 400\( \mu \text{m} \) wide channels used for delivering the catalyst slurry. Figure 2-9B is a scanning electron micrograph of a cross-section of the inlet channels where they meet at the main reaction chamber. At the outlet of the 2-cm-long reaction chamber is a series of posts etched in the silicon which are used to retain the packing material. Figure 2-10 is a photo micrograph of the single channel reactor filled with activated carbon catalyst.
Figure 2-8. Reaction channel outlet design. A) Schematic indicating the position of the filter unit immediately upstream of the exit port. B) SEM of a cross-section of the filter structure.
Figure 2-9. Single-channel multiphase microreactor inlet design. A) Schematic indicating the design for splitting a single gas inlet into 4 streams, a liquid inlet into 5 streams, and interleaving the inlet streams until they meet at the reaction channel. B) SEM cross-section of 9 inlet channels.
Figure 2-10. Photomicrograph of single channel micro reactor. (Courtesy of Felice Frankel)
2.3. Single Channel Reactor Fabrication

Details for the fabrication process can be found in chapter 3, but are described here briefly. The fabrication process for the single channel reactor involves two etch steps and an anodic bond. The topside channels are first formed in the silicon substrate by using a time-multiplexed inductively coupled plasma etch process. [61] This etch process is the key technology which allows the definition of small high-aspect ration features for all of the devices of this thesis. The depth of the channels is controlled by timing the etch to approximately 300 μm. As seen Figure 2-8, a loading effect in the etch process causes the 25 μm wide channels to be approximately 20% more shallow than the main reaction channel. The wafer is then patterned from the bottom side to allow ports to access the various channels. The final step in the process is to cap the channels with Pyrex glass using an anodic bond.[62] The wafer is then diced into twelve reactors 1.5 cm X 3.5 cm. Prior to the anodic bond, the silicon wafer can be treated to a thermal oxidation in order to coat the reaction channels with a protective silicon dioxide layer. The oxidation improves the anodic bond process as measured by the reduced size of defects (non-bonded areas).
2.4. Packaging and Experimental Set-up

Each reactor chip produced by the above microfabrication procedures is, in effect, a sliver of silicon and glass with ports on the bottom side requiring external connection. Interfacing the chip with the macro-world of fluid flow and data acquisition is the subject of packaging.

![Diagram showing packaging setup](image)

**Figure 2-11.** Fixture for interfacing the chip with external fluidics. A steel block is machined with ports for fittings connected to external tubing and ports that align with ports on the chip. An aluminum plate compresses the chip against a gasket, forming the seal.

The capabilities of these silicon microfabricated microreaction devices, in terms of upper temperature and pressure limits, are determined entirely by the engineering of the macroscopic interface, namely the packaging. A number of constraints govern the nature of the packaging. First is an adequate fluid seal. Pressures generated, as a result of forcing fluids through the microfluidic channels, can be as high as 50-100 PSI. The second constraint is temperature. Most pharmaceutical processes rarely require temperatures in excess of 200 ºC, but reactions for fine and specialty chemicals.
manufacture can require much higher temperatures. Another constraint is materials compatibility. An all-glass interconnection method would be ideal for most cases, but there is no convenient way to break and rejoin glass connections as there is with metals. As such, the materials need to be compatible with a range of solvents and gases at elevated temperatures.

Figure 2-12. Photograph of steel interface fixture. Left) arrangement of ports. Right) Assembled with microreactor and aluminum compression plate (with cartridge heaters).

The approach employed in this study was to use a compressed elastomeric gasket to form the seal between the chip and a metal fixture with channels (1/32" diameter) connecting to ports for standard high pressure metal fittings (Figure 2-11). O-rings were attempted, but two shortcomings were apparent. One was that the force of compression was unevenly distributed throughout the brittle silicon-glass chip, causing the chip to break. The other shortcoming was the size of the o-ring itself. A design employing o-rings would require ports with a spacing of at least 3-5 mm. When the size of the chip is 10 mm × 40 mm, this separation can be problematic when several connections need to be
made. On the other hand, a gasket that contains 1/16” diameter holes requires less spacing between ports and provides a more even counter-force during compression. The result of this approach for packaging is that the properties of the gasket material ultimately determine the limitations of the reactor.

Figure 2-13. Assembled reactor package. Multichannel reactor is visible through plexiglass cover-plate allowing visualization of microchannel flow.

Figures 2-12, 2-13, and 2-14 show the experimental setup and packaging for the micro packed-bed reactor. The silicon-glass reactor is compressed against a thin elastomeric sheet (0.8mm thick Viton™) to form a fluidic connection to the stainless steel base that was machined for standard high-pressure fittings. The cover plate, which compresses the chip, can either be aluminum with cartridge heaters (3.2mm, 25watts,
Omega, Stamford, CT) for temperature control, or plexiglass for visualization. Thermocouples (0.25mm, type K, Omega) are inserted into 400µm channels of the microreactor. In-line pressure transducers (Omegadyne, Stamford, CT) connected with a low-volume stainless steel T type connector (Upchurch Scientific) measure the pressure. A mass flow controller (Unit Systems) delivers the hydrogen while a syringe pump (Harvard Apparatus PHD2000) delivers the liquid reactant. Fractions of the effluent are collected and analyzed off-line using a Hewlett-Packard 6890 GC with a mass selective detector. Flow visualization is obtained with the use of a Leica MZ12 stereomicroscope connected to a Cohu CCD camera positioned directly above the plexiglass compression plate.

Figure 2-14. Experimental set up. All fittings and tubing are 1/16" stainless steel.
Although this approach for interfacing the chips is convenient in terms of testing multiple devices, it nevertheless places severe limitations on the testing of the devices. The gasket material determines the upper temperature limit (\(T_{\text{max}} = 200^\circ \text{C}\) for Viton, \(T_{\text{max}} = 300^\circ \text{C}\) for Kalrez). The compression seal, as well as the fluids employed, determine the upper pressure limit. The packaged reactor has been tested to 150 psi (10 atm) before a sudden leakage of hydrogen became significant. (\(P_{\text{max}} = 10 \text{ atm}\))

We have loaded different materials into the microreactor including glass microspheres (MO-Science Inc., MN), polystyrene beads, and catalyst powders. All chemicals and catalysts, unless otherwise noted, were used as obtained from Sigma-Aldrich (Milwaukee, WI). Using standard sieving equipment, a 50-75\(\mu\)m fraction was filtered from the catalyst powder and a slurry formed using ethanol. The slurry was delivered to the microreactor using the 400-\(\mu\)m-wide side channels (Figure 2-10). Once the reactor was loaded with material, the catalyst inlets were closed by either substituting a different gasket or capping the external fittings.
2.5. **Pressure Drop Results**

The pressure drop in the microreactors was first characterized for single phase flow. For multiphase flows, predicting the two-phase pressure drop is considerably more complicated, requiring a knowledge of the relative gas and liquid volumes in the reactor. The relative volumes of the two phases in the reactor volume are determined by the fluid properties as well as the relative flow rates. Measuring the gas and liquid hold-ups (the relative volumes occupied in the reactor) in the packed-bed microreactor is problematic using conventional gravimetric methods. Optical microscopy is difficult for the packed-beds owing to the 3-dimensional nature of the flow. In the microstructured reactors of chapter 6, two-phase flow is more easily observed.

The single channel reactor was filled with 50-71 μm particles of glass and activated carbon. For various flow rates of ethanol, the pressure was recorded and is plotted in Figure 2-15. Figure 2-15 also compares the results for the single channel reactor pressure drop with the Ergun equation. Differences between the experimental values and the predictions are reasonable given the uncertainty in the void fractions for the micro packed-beds. Thus, it appears that the use of the Ergun correlation can be extended to microreactors.
Figure 2-15. Measured pressure drop for ethanol in a packed single-channel microreactor. The results compare favorably to the pressure predicted by the Ergun equation for a void fraction of 0.4. The error bars represent one standard deviation with 3 samples for each data point.
2.6. Application of the Single Channel Reactor to the Synthesis of Phosgene

2.6.1. Introduction

Candidate chemical systems for microreaction technology are those involving fast and exothermic reactions. In addition, reactions that involve the production of toxic and hazardous chemicals would benefit from distributed, on-demand synthesis. A portable, miniaturized platform for generated these dangerous compounds would alleviate the risks associated with storage and transportation. Furthermore, testing chemistries with these compounds would be inherently safer if the amounts required for the experiment were greatly reduced. The possibility of miniaturized plants for safer operations has recently been reviewed.[63] Phosgene (COCl₂, carbonyl dichloride), is such a toxic intermediate used commercially in fine chemicals and pharmaceutical synthesis. Phosgene is manufactured in the gas phase from chlorine and carbon monoxide using an activated carbon catalyst:

\[ \text{Cl}_2 + \text{CO} \rightarrow \text{COCl}_2 \quad \Delta H = 26 \text{ kcal/mol} \]  

The reaction is fast and exothermic.[64, 65] The toxicity of phosgene is such that it was used as a chemical warfare agent in World War I and has a lethal exposure limit to humans of 400-500 ppm-minutes. Phosgene is produced commercially on a large scale (3 billion pounds per year) for use in manufacturing isocyanates, polycarbonates, polyurethane foams, pharmaceuticals and herbicides. Processes using phosgene require specialized cylinder storage, environmental enclosures, pipelines, fixtures under negative pressure, and significant preventative maintenance. These difficulties also apply to any
involving phosgene. Moreover, phosgene is under a variety of transportation restrictions.
As a consequence, most phosgene is consumed at the point of production.[66] Off-site production often necessitates out-sourcing not only the phosgene synthesis, but also a set of sequential processing steps in order to get to a safe, transportable compound. Microchemical systems stand to provide an opportunity for flexible point-of-use manufacture of chemicals such as phosgene. Reactors operating in parallel can be turned on or off as needed to maintain as close to zero storage as possible. Single reactor failures would lead to extremely small chemical releases.

In this work, I present phosgene synthesis in a silicon based micropacked-bed reactor as an example of the potential for safe on-site/on-demand production of a hazardous compound. Preliminary productivity values are presented. The versatility of microfabricated reactors is demonstrated for hazardous and corrosive gases such as chlorine through the use of a glass-like protective coating that is formed during the reactor fabrication process. The increased heat and mass transfer characteristics, which provide inherent safety and increased productivity in chemical synthesis, are also explored as advantages in the extraction of chemical kinetics. The pre-exponential factor and apparent activation energy for phosgene formation are determined to demonstrate the utility of micropacked-bed reactors as laboratory research tools.
2.6.2. Chemical Compatibility of Silicon/Glass

Chlorine reacts with silicon, particularly at elevated temperatures. Consequently, microreactors made from silicon would be chemically attacked, eventually dissolving to such an extent that reactor failure would occur. Figure 2-16A shows the deleterious effects of reacting chlorine in a silicon device at 250 °C. The reactor inlets and channels are severely etched. Note that the etching occurs in the vicinity of where the packed bed of catalyst begins. This position is where the pressure, the concentration of chlorine, and the temperature are likely to be the highest with the fastest release of heat occurring at the start of the reaction. Etching does not initiate directly at the inlets upstream, suggesting that there is a temperature increase near the start of the packed-bed. In contrast, the reactor with a thermally grown silicon oxide layer (Figure 2-16B) shows no

Figure 2-16. A) Silicon reactor after exposure to chlorine at 250 °C. B) Silicon reactor with 5000Å oxide layer after exposure to chlorine at 250 °C for 6 hours. The oxide layer prevents the etching of the silicon by the chlorine.
visible change after 6 hours of continuous experiments. The advantages of silicon/glass as a reactor material are evidenced through this high temperature reaction. Not only is the silicon thermally conductive and capable of withstanding high temperature operation, but the ability to deposit thin films of alternate materials extends the range of materials compatibility.

2.6.3. Phosgene Reaction Results

No temperature increase could be measured upon switching flow from the bypass line to the reactor. This thermal uniformity is expected because single crystal silicon has a large thermal conductivity (150 W/m K) and readily dissipates heat from the packed-bed. The thermal mass of the stainless-steel packaging is many orders of magnitude larger than the reactor and provides a significant heat-sink. Likewise, the energy provided by the cartridge heaters to maintain the temperature of the reactor/packaging is orders of magnitude larger than the energy generated from the reaction. No deactivation as reported by Shapatina et al.[67] was observed during the experimental time-scales (6-10 hours) possibly due to the high level of purity in the gas feeds.[67] No side-products were observed in a full mass spectrum scan, presumably as a result of suppressing hot-spots common in larger reactors and using high purity feeds. Products such as silicon tetrachloride, which would form if chlorine reacted with silicon, were also not detected. The experimental results are summarized in Figure 2-17.

Isocyanates are derived from reactions of phosgene with amine precursors. The reactions are highly exothermic, and selectivity towards the desired products is strongly governed by reaction conditions, in particular, temperature.[65] Following a procedure
for the synthesis of cyclohexylisocyanate [68], phosgene generated by the microreactor at complete conversion was used to drive a small bench scale experiment. Phosgene was continuously bubbled through a solution of cyclohexylamine and toluene in a 50mL reaction flask. Generation of cyclohexylisocyanate was demonstrated, with complete conversion of the amine reactant. Even with volumes as small as 50 mL, the flask temperature rose 50 °C without external cooling, severely impacting selectivity. Integrating a microfabricated gas-liquid reactor performing the amine phosgenation with the microreactor producing phosgene into a single microchemical system would give better control over selectivity. Moreover, the phosgene would be consumed in the same device as it is produced further reducing the hazards of working with the toxic compound.

The apparent activation energy from the experiments of 7.6 kcal/mol compares with the 8.6 kcal/mol reported by Shapatina et al.[69] The rate constants extrapolated from the microreactor also favorably compare to the previously published values. The data falls on a straight line, even at the higher temperatures, giving further evidence for the lack of mass transfer limitations.
Conversion of Cl₂

Phosgene production rate:
1.1 g/hr
(Single channel)

Eₜₐₓ: 7.9 kcal/mol
Shapatina: 8.6 kcal/mol

Figure 2-17. Experimental results for phosgene synthesis in a single channel microreactor. Catalyst is 1 mg of activated carbon, flow rate of phosgene is 4 sccm, with stoichiometric feed of chlorine and carbon monoxide.
2.7. Single Channel Reactor Summary

The first step in the design of the microreaction devices for heterogeneous chemistries was the incorporation of the catalyst. It was determined that thin films of catalytic materials, while active for some fast gas-phase reactions, would be insufficient for some of the slower gas-liquid catalytic reactions. The simple approach to catalyst integration was to incorporate conventional catalyst powders by using discrete particle size fractions and loading into a device with a suitable filter. The dimensions for the catalyst particles, as well as the dimensions for the reaction channel, were determined in part by estimating the pressure drop using the Ergun equation. The measured pressure drops matched very well with predictions.

The method of mixing the two reagent streams on chip was motivated by results from a liquid-liquid mixing device. Interleaving laminated streams served to reduce the diffusional length scale as well as provide an even distribution of the reactants at the start of the reaction channel. Separate inlet channels were provided in order to load the particles into the reaction channel. The entire device was packaged using the compression of an elastomeric gasket to form the fluidic seal.

The gas-phase synthesis of phosgene was performed in the single channel reactor with complete conversions achieved at 200 °C. The phosgene reaction is fast and very exothermic, yet precise temperature control was achieved for the range of temperatures investigated. The determined activation energy agreed with literature values, indicating the absence of mass transfer effects. A thermal oxide layer on the silicon was sufficient to prevent corrosion of the silicon by the chlorine gas.
3. "Multi-channel" Reactor Design

Two important conclusions regarding microreactor design come out of the single channel reactor study. First, is the geometrical influence on pressure drop, the second is the necessity for adequate reactor volume for practical throughputs. This chapter and the design presented, is an extension of the last: multiple reaction channels are configured to operate in parallel. The reasons for doing so are discussed as well as the modifications to the fabrication process. The multiphase reaction involving catalytic hydrogenation is introduced to analyze quantitatively the mass transfer characteristics of the microreaction device. Gas-liquid flow behavior is characterized and compared with flow phenomena at the macro scale.

Based on equation (2-3), for a given volume of packing with constant residence time, a short, large diameter reaction channel would minimize the pressure drop. If reactions are operated such that there are no mass transfer limitations, then the capacity for conversion depends on the amount of catalyst and not on the specific geometry. The problems with operating such a design are obtaining an even distribution of reactants over the inlet diameter and controlling the temperature profile. Since the temperature of most tubular reactors is controlled through the exterior radial walls, a large diameter reactor will become increasingly hindered by radial gradients in temperature. Therefore, splitting the flow into multiple channels so that the effective cross-sectional area is large will ultimately reduce the pressure drop while maintaining the same reactor throughput and high surface-to-volume ratio. Microfabrication methods have the potential for efficiently realizing such a reactor design; one that reduces mass transfer limitations.
ensures thermal uniformity and employs a reactor geometry which reduces the pressure drop.

3.1. Microfluidic Design

In order to construct a chemical system on a chip, the following features were desired: a) the ability to mix multiple reagents, whether of the same phase or different phases b) the ability to heat the reaction zone and measure the temperature and c) the ability to incorporate catalytic activity whether by standard catalytic particles or integrated catalytic layers. Two similar devices were designed toward this end. Both consist of multiple reaction channels connected in parallel. In the first design, the channels (300 μm deep, 625 μm wide, 20 mm long) are empty and contain a filter structure near the exit to retain a packed-bed of catalytic particles. The second device contains staggered arrays of 50 μm columns within the channels to provide both catalyst support and static mixing. This second device is presented in the next chapter. The results with the multichannel packed bed reactors lends motivation for the microstructured reactor.

The first function for any of the reaction devices described in the present work is to mix two reagents on-chip. The approach taken here uses the continuous flow split and mix strategy. Mixing multiple phases, such as a gas and liquid, at the micro scale is more problematic: interfacial forces cause the phases to rapidly coalesce. Keeping the fluids dispersed in order to reduce diffusional length scales is considerably more difficult as compared to mixing two liquids of similar physical properties. Nevertheless, improved gas-liquid contacting has been demonstrated in this and other microchannel applications.[41, 70]
3.1.1. Overcoming Surface Tension in Microchannels

As the dimensions of the device shrink, capillary forces have more of an impact on fluid flow. The Young-Laplace equation, \( \Delta P = 2\gamma/r \), can be used to estimate the minimum pressure needed to overcome surface tension (\( \gamma \)) effects for a gas-liquid interface in a small channel. [71] For a 10 \( \mu \text{m} \) channel radius and water (\( \gamma = 72 \text{ dyn/cm} \)), \( \Delta P = 0.14 \text{ atm} \). Therefore, the dimension for the inlet mixing channels (25 \( \mu \text{m} \) wide) is not so small that surface tensions effects would become prohibitive. This consideration does not include the forces required to overcome frictional resistances of two-phase flow in capillaries. In that case, the pressure drop depends on the velocity, relative volumes of the two phases, and the length of the channel in addition to channel radius. Theoretically, microfabrication methods could allow the construction of channels smaller than a micron. For a channel diameter of 0.2 \( \mu \text{m} \), the pressure required to overcome surface tension is severe: 14 atm. Therefore, the scaling of the inlet channels for multiphase mixing is dictated by these surface tension effects: a 10 \( \mu \text{m} \) characteristic radius is sufficiently large that surface tension is not severe, and yet small enough to take advantage of diffusional processes.

Even though surface tension is not restricting the flow in the microchannel contactor, it nevertheless dictates the nature of two-phase flow. The fluid dynamics of the two-phase flow depend on the relative effects of surface tension and inertial forces. Two dimensionless numbers have been used to establish this relationship and appear in a number of correlations of multiphase fluid dynamics and mass transfer. The Capillary number, \( Ca = \mu_L V_L/\sigma \), provides a ratio of the inertial forces to the capillary forces for two-phase flow, where \( \mu_L \) is the viscosity of the liquid, \( V_L \) is the velocity and \( \sigma \) the
surface tension. For the range of flow rates and materials used in this study, $1 \times 10^{-5} < Ca < 1 \times 10^{-3}$. In the context of packed beds, the Webber number, $We = \frac{V_L^2 D_p \rho}{\sigma}$ also provides a ratio of inertial forces to interfacial forces, where $D_p$ is the diameter of the particles and $\rho$ is the density of the liquid. For the small 50 μm diameter particles in the reactors here, $1 \times 10^{-7} < We < 1 \times 10^{-3}$. Both of these dimensionless numbers indicate that surface tension is the driving force governing the nature of the two-phase flow.
3.1.2. Device Layout

The overall device consists of two bonded silicon layers and a glass layer to cap the top most channels. As seen in figure 3-1, an array of 10 reaction channels are fabricated in silicon and connected through an on-chip microfluidic manifold. Reagents enter and exit the chip from the ports on the bottom-side, underneath the chip. The gas inlet (figure 3-1, cross-section A) is divided into 10 channels whose widths vary, depending on the length, to ensure an even distribution of flow. These ten streams are further divided into 4 streams (25 μm wide) before entering the ‘mixing zone.’ The second inlet for the liquid is split into multiple inlet channels (25 μm wide) in the bottom silicon layer (figure 3-1, cross-section B). In this way, the 90 gas and liquid inlet streams are interleaved in an alternating fashion. The second layer of silicon is required to manifold the second inlet without overlapping the different sets of streams. Figure 3-2 is an enlarged view indicating the alignment of adjacent channels such that the two reagents will not mix until they have reached the reaction channels. These inlet streams proceed until they meet at the ‘mixing zone’, just prior to the reaction channels.

The 10 reaction channels are 2 cm long, 600 μm wide, and 300 μm deep. Each of the ten channels is connected by a 500 μm wide channel running perpendicular near the inlets (figure 3-1, at cross-section C). This intersection is where the multitude of inlet streams first meet and is considered the ‘mixing zone.’ This channel also allows the catalytic particles to be loaded into all ten channels simultaneously.

Separate ports and inlet channels for the catalyst are required because the inlet streams (25 μm wide) are meant to prevent a back-flow of catalyst during operation. The catalyst is loaded as a slurry, and as such requires a certain velocity to keep the particles
suspended. Two different ports for the catalyst slurry are necessary: as the device is filled with particles, the pressure drop increases and it becomes increasingly difficult to generate the velocities needed to drive the particles. With two catalyst inlet ports however, a cross flow of catalyst slurry can be easily attained and the particles steadily loaded into the channels. This ability for cross flow also helps to ensure an even loading of particles among the ten channels.

At the end of the 2-cm-long channels are filter structures consisting of 40 μm wide columns with a separation gap of 25 μm. After the filter, the fluids exit via a 400 μm diameter port to the bottom silicon layer, where all ten exit streams are collected to a single port (figure 3-1, cross-section D). The difference between the packed-bed device and the microstructure one is simply the arrays of columns patterned into the channels; all the other fluidics are the same.
Figure 3-1. Top, plane view of multichannel reactor and point of cross-sections. A) Gas inlet. B) Liquid Distributor. C) Catalyst inlets. D) Exit port manifold.
3.2. **Heater Design**

To test the potential for integrated temperature control in an individual reaction device, thin film resistors were designed and tested. Thin film resistive elements have been used in conjunction with membrane reactors, where the thermal isolation of the membrane allows high temperatures (>700 °C) to be reached. [47] In this application, the ultimate temperature requirement is much lower (<300 °C) but heating of the entire chip and fluid is necessary and heat loss to the environment is substantial. Incorporating heating elements also allows for experimental characterization of the thermal properties of microchemical devices before testing highly exothermic chemical reactions.
The amount of energy required to raise the temperature of the fluids for a given flow rate can be used as a first order approximation for the size of the heaters. The energy required to raise the temperature from 25 °C to 90 °C of water flowing at 0.1 mL/min. is 0.5 Watts,

\[ q = \dot{m} \cdot C_p \Delta T \]

where \( \dot{m} = Q \cdot \rho = 0.1 \text{ g/min}. \) and \( C_p = 4.2 \text{ J/(g K)}. \) For hydrogen flowing at 100 sccm, assuming a density of \( 9 \times 10^{-5} \text{ g/cc (30°C)}, \) and \( \Delta T = 300^\circ \text{C}, \) q = 0.6 Watts.

For hydrogen, \( C_p = 14.3 \text{ J/(g K)} \) which is substantially larger than Nitrogen \( (C_p = 1 \text{ J/(g K)}) \).

As will be shown later, convective heat losses from the external surface of the chip is somewhat larger (1.3 W at 80 °C). While trying to maximize the power delivery to the chip, the constraints on the design were the thickness of the metal film and the maximum current density. Thicker films are desired to allow higher current flow, but the metal layer must be thin enough to allow a fluidic seal between the glass and silicon layers using the anodic bond. Here, films 1000 Å in thickness did not prevent the glass wafer from bonding and sealing to the silicon. The maximum current density before electromigration serves to degrade the film can be taken as approximately \( 1 \times 10^{-6} \text{ A/cm}^2 \text{ s} \) [47].

**Test Device**

The resistance characteristics of titanium/platinum films were tested using a test pattern on a single channel reactor design. Figure 3-3 shows the layout of the heater. A film, 600 μm wide, 6 cm long, 1000 Å thick, was deposited. A smaller test pattern to
simulate a temperature sensing film was also used. Figure 3-4 shows a meandering pattern with a line 25 µm wide.

![Diagram showing platinum heater connections and inlets/outlets](image1)

**Figure 3-3.** Single channel reactor with integrated heater. A single line (500 µm wide) with 4 segments meanders along the length of the reaction channel.

![Diagram showing resistive temperature sensor](image2)

**Figure 3-4.** Resistive temperature sensor at the exit of the reactor.
The resistance of the heater at 25 °C was 262 Ohm, giving a resistivity of 0.26 Ohm µm. This was slightly higher than the known resistivity of platinum (0.11 Ohm µm). This could be due to insufficient annealing of the platinum after e-beam deposition as well as resistance at the contacts. Figure 3-5 is a resistance vs. temperature plot showing linear behavior to at least 125°C. One of the advantages of platinum as a temperature resistive element is the large range of linearity between resistance and temperature.

The temperature resistivity coefficient, $\alpha_T$ was calculated to be 0.0021 °C$^{-1}$, defined as:

$$\text{Resistance}(T) = \text{Resistance}(T = 25\text{C}) \cdot (1 + \alpha_T \cdot T)$$

This compares with values of 0.0029°C$^{-1}$ reported for platinum films on silicon nitride membranes.[47]

![Graph showing temperature vs. resistance](image)

**Figure 3-5.** Temperature dependence of the resistance for the heater. Error bars represent approximately 5% error in the resistance measurement.
Heater design for the multiple channel reactor

Based on the measured resistivity characteristics of titanium/platinum films on the test structures above (0.26 Ohm μm), the meandering pattern of Figure 3-6 was chosen so that the total resistance would be near 100 Ohm. This would allow the heaters to operate near 10 watts with a reasonable potential (30 V) and still be within the current density limits. The lines (600 μm wide) form two parallel resistance paths 5.4 cm length each. For the dimensions of the heater (600 μm X 0.1 μm) and the assumed maximum current density, the maximum current allowed is 0.9 A, or 30 W. The heater lines were positioned in such way to ensure an even distribution of heat among the ten channels. Each of the ten channels is separated by an island of silicon 625 μm wide. These islands serve to provide mechanical stability for the entire chip, provide more surface area for the anodic bond, and provide a conduit for heat from the thin film heaters to the rest of the silicon.

Figure 3-6. Layout for heater lines and temperature sensor. The heater line (500 μm wide, 1500 Å thick) has two parallel segments running along the length of the channels.
3.2.1. Thermal Performance Characterization

Resistivity of the titanium/platinum films depended upon the conditions of the post deposition anneal. Annealing for 3 hours at 500 °C yielded a resistance of 125 +/- 4 Ohm or a resistivity of 0.26 Ohm μm. If this was followed by an anneal at 650 °C for 2 hours, the resistance dropped to 91 +/- 3 Ohm or a resistivity of 0.18 Ohm μm. This compares to the resistivity of pure platinum, 0.11 Ohm μm.

Power-temperature characteristics were evaluated to determine the feasibility of using thin film heaters as a temperature source in a microchemical system. The heaters were tested and their performance in controlling the temperature of the chip was entirely dependant upon the packaging scheme. Using the packaging scheme depicted in figure 2-13, the thin film heaters were unsuccessful in rapidly bringing the reactor to a desired set-point. Since the reactor is tightly sandwiched between two metal fixtures, the area for external convection is enhanced and the total thermal mass is large. Several hours were required to bring the packaged system to a set-point of 70 °C with a power input of 15 watts.

Alternative packaging schemes, such as tubing attached directly to the chip, could improve the situation.[72] This was tested by suspending the chip both in air and wrapped in a fiberglass insulation material. For a chip suspended in air, a power input of 2.2 watts produced a steady temperature of 125 °C, while a chip with insulation and a power input of 4 watts produced a temperature of 300 °C. Figure 3-7 shows the temperature versus power behavior for the single channel reactor.
Figure 3-7. Resulting temperature for a given power input using an integrated thin-film heater in a single-channel reactor.

3.2.2. Heat Transfer for a Free Standing Microchip Reactor

As a first estimate for a heat transfer coefficient for the silicon/glass microreactor in air, a control volume can be considered where the heat generation is entirely from the current load and the heat removal is due to external convection:

\[ Q = \bar{h}A(T - T_A) \]

For a power of 2.2 watts, a steady temperature of 120 °C, an external area of the chip of 7 cm², the average heat transfer coefficient is calculated to be 31.4 J/(K s m²).
To determine if there is a temperature gradient within the chip, the Biot number is calculated which represents the ratio of resistance to heat transfer in the external boundary layer versus conduction within the chip:

\[
Bi = \frac{hL}{2k}
\]

where \( L \) is the characteristic length for conduction, here taken as the thickness of the chip, and \( k \) is the thermal conductivity. The Biot number is calculated for the following values: \( h = 31 \, \text{J/(K m}^2 \text{s)} \), \( L = 1 \, \text{mm} \), \( k \) (silicon) = 150 \, \text{J/(K m s)} \), \( Bi = 1 \times 10^{-4} \).

Even for a lower thermal conductivity, such as that for glass (1 \, J/(K m s)) the Biot number is still much smaller than one, indicating that all of the resistance for heat transfer is external to the chip and consequently thermal gradients within the chip are unlikely to exist at steady state. This allows a lumped model to describe heat transfer from the chip. Furthermore, with this estimate of the heat transfer coefficient, thermal gradients within the reactor can be determined for various geometries of the heater segments. In the next section, a sample calculation is provided showing the temperature gradient for a sample heater geometry.

To assess the capacity for dissipating heat without active cooling and to determine the characteristic time scale for temperature change, a time profile for cooling was measured. Figure 3-8 is a time profile for temperature relaxation. At time zero, power was removed and the chip allowed to cool to room temperature. The chip was free standing, in that there was no insulation or packaging which would have affected heat
transfer. It is assumed that heat transfer through the thermocouple and wire leads was negligible relative to heat loss through the surface of the chip.

![Temperature Decay Curve](image)

**Figure 3-6.** Temperature decay with non-insulated chip. The reactor was heated to the initial temperature with the integrated heaters and then allowed to cool to room temperature. The thermal response time is measured to be 1.6 minutes.

Temperature was recorded continuously using LabView. Initially, the power supplied to the reactor was 2.2 W, producing a temperature of 120 °C. For the unsteady temperature decline with removal of the current, conservation of energy requires:

\[
\rho C_p \frac{dT}{dt} = -\nabla \cdot q
\]

(A3-1)

Averaging and integrating over the entire volume of the reactor gives,

\[
\overline{T} = \frac{1}{V} \int T dV
\]

(A3-2)
\[
\int \rho C_p \frac{\partial T}{\partial t} dV = -\int (\nabla \cdot q) dV
\]
(3-3)

\[
\rho C_p V \frac{\partial T}{\partial t} = -hA(T - T_A)
\]
(3-4)

\[
\int \rho C_p \frac{\partial T}{\partial t} dV = -\int (n \cdot q) dA
\]
(3-5)

Solving for the temperature as a function of time provides the time scale for the temperature decay:

\[
\frac{T - T_A}{T_0 - T_A} = e^{-\frac{t}{\tau}}
\]
(3-6)

\[
\tau = \frac{\rho C_p V}{hA}
\]
(3-7)

A plot of the natural logarithm of the temperature versus time will give a straight line, the slope of which is the time scale and can be used to determine the heat transfer coefficient. Figure 3-9 shows the linearized data where \(\Theta\), the dimensionless temperature variable, is defined as in equation 3-6. The slope gives the time constant, \(\tau = 1.6\) minutes and \(hA = 0.014\ J/K/s\). For a surface area of 7cm\(^2\), \(h = 20\ J/K/m^2\).
Figure 3-9. Linearized temperature versus time profile (data from Figure 3-8). The measured slope provides the heat transfer coefficient.

3.2.3. Discussion: Heat Exchange in Microchemical Devices

The results of the various packaging schemes on the thermal performance of the microreactor serve to illustrate the trade-off between control and efficiency. The heat losses to the environment as a result of the large surface areas can be significant. This attribute can be used as a means for dissipating the heat of a reaction without active cooling. If heat transfer is between the chip and air, then the steady state temperature for a power input of 1.3 watts was 80 °C. Considering the phosgene reaction, one that was both fast and exothermic, the heat generation for a single channel reactor at 100% conversion is 0.4 Watts (rate = 1.1 g/hr, ΔH=110 kJ/mol). This amount of heat is easily dissipated without active cooling given that the reaction requires a temperature of 250 °C. As a result of this imbalance between the power required to heat the chip (or conversely
the large amount of heat dissipation) and the heat potentially generated by the reaction, a large amount of control is afforded over the process. Temperature is determined entirely by the power input by the heaters, not by the heat generated by the reaction. The trade-off is that the reactor is operating inefficiently due to the large amounts of energy lost to the environment.

If instead the chip is thermally isolated, then less power is required for a given temperature. A power input of 3 watts now generates a temperature in the reactor of 250 °C instead of 150 °C, see Figure 3-7. The reactor operates more efficiently, but at the expense of control since the reaction now generates heat at rates which are comparable to losses due to external convection. Depending upon the application, either one of the these modes of operation may be desirable.

Citing the phosgene example above, if the reaction was now performed in a 10 channel device, the rate of heat generation would now be at 4 watts. For a non-insulated chip, this would produce a temperature close to 250 °C, the required temperature of operation to achieve the cited rates of reaction. According to this calculation, a multichannel reactor could perform the phosgene reaction without the need of either on-chip cooling or heating. This suggests that individual microreactors could be tailored to the chemical reaction at hand. The reaction volume in a chip could be adjusted such that the heat generated by the reaction is exactly that required for the intended temperature of operation. Not counting the energy produced by the reaction, this would be the most efficient way to operate a reactor. For the phosgene reaction, this would be impossible at any other scale. At a larger scale, the external heat transfer coefficient may be the same,
but the surface area per volume ratio would be much smaller and as a result, the total amount of heat transfer would be reduced relative to the heat generation of the reaction.

3.2.4. Thermal Uniformity Calculation

In the design of the heater for the multichannel reactor, several design options were available, and so a calculation was performed to arrive at an optimum heater geometry. The calculation involved determining the temperature gradient between two parallel heater elements on a silicon chip. For a given temperature drop, the maximum spacing between the elements can be estimated.

The heat transfer coefficient from the chip surface was estimated from experiments. The value used here (30 J/K m2 s) is for a non-insulated chip, where the heat transfer will be most severe and the temperature gradients the largest.

The system to be modeled can be seen in Figure 3-11. Thin platinum films meander along the silicon glass interface. Applying a current through the films allows the chip to be resistively heated. The calculation will show that for a heater spacing of no more than 1 cm, the temperature difference from the portion of the silicon directly next to the heater to the portion of the silicon in the center will be smaller than 10K.
Figure 3-10. Model for determining temperature uniformity.

The Biot number based on a chip depth, $W$, of 1 mm and the thermal conductivity of silicon is:

$$Bi = \frac{hW}{k} = 1.3 \cdot 10^{-4}$$  

(3-8)

Consequently, most of the heat transfer resistance is external to the chip. This allows for the fin approximation, where the temperature is uniform in the $z$ direction and varies along $x$. (Deen, 3.3-19)

Assume that the heat source can be treated as a uniform flux in the $x$ direction, and thereby reduce the problem to one dimension as in Figure 3-12. Also assume that edge effects can be neglected, as the predominant surface area is the top and bottom planes of the chip.
Figure 3-11. 2-D model for temperature uniformity profile

From the energy conservation equation,

\[
\frac{d^2 \bar{T}}{dx^2} - \frac{2 \cdot h}{Wk} (\bar{T} - T_{am}) = 0
\]

(3-9)

(the factor of 2 comes from a heat flux at two surfaces (top and bottom))

substituting

\[
T = \bar{T} - T_{am}
\]

(3-10)

and

\[
X = \frac{x}{W}
\]

(3-11)

gives:

\[
\frac{d^2 T}{dX^2} - Bi \cdot T = 0
\]

(3-12)

subject to the boundary conditions:
(B.C. 1)

\[ k \frac{dT}{dX} \bigg|_{x=0} = -q \]  

(3-13)

(B.C. 2) (symmetry condition)

\[ \frac{dT}{dX} \bigg|_{x=L/2w} = 0 \]  

(3-14)

The solution to (3-12) has the form:

\[ T = C_1 \cdot e^{\sqrt{Bi} \cdot x} + C_2 \cdot e^{-\sqrt{Bi} \cdot x} \]  

(3-15)

Solving for the constants gives,

\[ C_1 = \frac{q}{\sqrt{Bi} \cdot k} \cdot \left( \frac{1}{1-e^{-2\sqrt{Bi}\gamma}} - 1 \right) \]  

(3-16)

\[ C_2 = \frac{q}{\sqrt{Bi} \cdot k \cdot (1-e^{-2\sqrt{Bi}\gamma})} \]  

(3-17)

\[ \gamma = \frac{L}{2W} \]  

(3-18)

For the conditions under which h was determined experimentally, the power through the heaters varied from 1-3 watts for a heater containing 4 segments 1.5 cm long.

To use the most extreme conditions for thermal non-uniformity, the calculation involves distributing the power into two heating segments, 2 cm long which are at opposite ends of the 1.5-cm-wide chip. (Figure 3-11). This would produce the most
drastic temperature change at the center of the chip. The temperature profile between two such elements is shown in Figure 3-13 for a power of 1 watt.

For a power of 10 watts and a separation of 1.5 cm the temperature change is 6.4K. Therefore, it can be concluded that the temperature of the chip is nearly uniform for any spacing between heating elements on a 1.5-cm-wide chip.

![Temperature Profile Between Two Heater Segments](image)

**Figure 3-12.** Calculated temperature profile for a power of 1 watt.
3.3. Fabrication Process

The fabrication process is presented first for the open channel design. The fabrication for the reactor with microstructured packing is similar with the exception of a few steps required for integrating porous silicon. This involves the use of a silicon nitride layer as mask for the electrochemical etching process which forms the porous silicon.

Thick resist (AZ4620, Hoechst AG) was spin coated to 10 μm thickness in order to pattern the two double-side polished silicon substrates. A contact mask alignment procedure was used (Electronic Visions EV 450 Aligner). The fluid channels were then formed in the silicon substrate by using a time-multiplexed inductively coupled plasma etch process using a Surface Technology Systems deep reactive ion etcher.[73] The depth was controlled by timing the etch to approximately 300 μm. For the conditions used, this required between 1 and 1.5 hours. Each wafer was then patterned from the back-side using infrared alignment and etched in a similar fashion. Due to slight variations in the etch rate, the etch from the backside was extended until all features 'broke-through' to meet the topside channels. This resulted in an over-etch of no more than 10 minutes, or 30 microns. These two silicon wafers were then cleaned (4:1 H$_2$SO$_4$:H$_2$O$_2$ 90 °C, followed by an RCA clean) and fusion bonded. The wafers were first contacted without vacuum (Electronic Visions AB1-PV Bonder) and then annealed at 1100 °C in nitrogen for 1 hour. After the bonding, an oxide coating was grown on the wafer stack using a wet thermal process at 1100 °C.

Separately, a Pyrex 7740 glass wafer (Bullen Ultrasonics) was patterned with a titanium/platinum film to create resistive heaters and temperature sensors. A thin
titanium layer served to promote adhesion between the glass and the platinum.[74] A simplified “lift-off” process was used where 1μm of thin resist (OCG 825-20cs, ) defined the metal lines in negative. After development, the Pyrex was subjected to an oxygen plasma for 1 minute to clear any residue prior to metal deposition. An e-beam evaporator was used to deposit first 50 Å of titanium followed by 1000 Å of platinum. Immediately following the deposition, the photoresist was removed by sonication in acetone for 10 minutes. Any metal/resist remnants were removed by a treatment with a resist strip (Nanostrip) for 10 minutes. The patterned glass/metal wafer was then annealed at 500°C for 3 hours. The resistive elements thus fashioned were used as is. Ultimately, it would be desirable to insulate these metal features from exposure to the reaction channels for applications involving corrosive reagents. The insulation of electrodes has been demonstrated elsewhere using thin films of polymers [18] or CVD oxides.[75] The glass wafer and the silicon wafer stack were next anodically bonded with the metal films toward the silicon. [62] An Electronic Visions AB1-PV bonder was used at the following conditions: 500°C, 800 Volts for 5 minutes. After this last bonding step, the wafer stack was diced to produce eight reactors (15 mm × 40 mm × 1.5 mm). Figure 3-14 is a photomicrograph of the inlet manifolds feeding into the ten microstructured channels.
Figure 3-13. Photomicrograph of inlet manifold for the ten-channel reactor. A) The inlet channel widths vary according to the length from the inlet port to the reaction channel in order to ensure a constant pressure drop and even distribution of fluid flow. B) Each of the ten reaction channels has an inlet manifold consisting of 9 channels distributing the gas and liquid phases.
3.4. Orientation and Gravitational Effects for Micro Multiphase Systems

To determine if the orientation of operation (horizontal or vertical) of the microreactor would have an influence on flow behavior, several criteria from the literature were consulted. Numerous studies have investigated the influence of gravity on two-phase flow in small channels or capillaries.[76] These microchannel studies involve both circular and rectangular cross sections, generally with a hydraulic diameter near 1 millimeter. Fukano and co-workers investigated flow regimes and flow regime transitions for two-phase flow in capillaries ranging in diameter from 1 mm to 26 mm.[76] Operating under identical conditions with exception to orientation, the authors concluded that two-phase flow is unaffected by gravitational effects for capillary diameters less than 5 mm.

The first criteria for the relative influence of gravity on flow is the Bond number, which represents the ratio of gravitational forces to capillary forces:

\[ Bo = \frac{D^2 (\rho_L - \rho_G) g}{\sigma} \]  

(1)

where \( D \) is the diameter of the channel, \( \rho_L \) and \( \rho_G \) are the densities of the liquid and gas respectively, \( g \) is the gravitational constant, and \( \sigma \) is the surface tension. For small Bond numbers, interfacial forces dominate and orientation or gravity has no influence. Bruaner and co-workers provided a criterion for the dominance of surface tension based on the Eotvos number, \( Eo \):[77]
\[ E\text{"} = \frac{(2\pi)^2\sigma}{D^2[\rho_L - \rho_g g]} > 1 \]  

(1)

For air and water, the surface tension is 72 mN/m, while for air and most organic solvents the surface tension is between 20 and 30 mN/m. Table 3-1 shows the calculated values for Bo and E\" for a range of channel diameters.

**Table 3-1. Calculated dimensionless Bond numbers (Gravity vs. Surface Tension)**

<table>
<thead>
<tr>
<th>D (mm)</th>
<th>(\sigma) (mN/m)</th>
<th>Bo</th>
<th>E&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>72</td>
<td>14</td>
<td>1.5</td>
</tr>
<tr>
<td>1</td>
<td>72</td>
<td>0.14</td>
<td>150</td>
</tr>
<tr>
<td>0.1</td>
<td>72</td>
<td>0.001</td>
<td>15,000</td>
</tr>
<tr>
<td>10</td>
<td>20</td>
<td>50</td>
<td>0.4</td>
</tr>
<tr>
<td>1</td>
<td>20</td>
<td>0.5</td>
<td>40</td>
</tr>
<tr>
<td>0.1</td>
<td>20</td>
<td>0.005</td>
<td>4,000</td>
</tr>
</tbody>
</table>

The conclusion is that even for a range in solvent properties, for a channel diameter of 1 mm or smaller, the Bond number is smaller than 1 and the criteria proposed by Bruaner is met. **Orientation, therefore, does not influence the two-phase flow behavior for the devices of this thesis.**
Furthermore, the influence of buoyancy effects can be considered. The dimensionless parameters that determine the relative influence of thermally induced density gradients to viscous forces are the Rayleigh number, $Ra$, and the Grashof number, $Gr$:

$$Ra = \frac{gL^3\beta\Delta T}{\alpha u} \quad Gr = \frac{gL^3\beta\Delta T}{v^2}$$

For water at room temperature, $\beta = 2.066 \times 10^{-4} \text{ K}^{-1}$, thermal diffusivity $\alpha = 0.0015 \text{ cm}^2/\text{s}$, and the kinematic viscosity $v = 0.01 \text{ cm}^2/\text{s}$. For $L = 1 \text{ mm}$ and $\Delta T = 1 \text{ K}$, $Gr = 2$ and $Ra = 14$. Critical values for the Rayleigh number, where instabilities begin to occur, are near $1 \times 10^3$. [78] Given the small length scales involved, it is increasingly difficult to maintain even minor temperature gradients, so that free convection is unlikely to play a significant role in flow behavior.

### 3.5. Summary of the Multichannel Reactor Design

Photolithography allows the design of complicated fluidic networks at no additional cost in terms of fabrication time or equipment. The multichannel reactor of this chapter is an example of a microfluidic design which makes full use of the ability to construct complex fluidic manifolds and features. Ten identical reaction channels are connected in parallel and a fluidic distribution system has been designed to allow the simultaneous loading of catalyst particles and the even distribution of reactants among the ten channels. The inlet manifold for the reactants consists of 90 individual channels.
(25 mm wide, 300 mm deep) feeding into the reaction channels. Such a fluidic design would be difficult at best, to fabricate using conventional means.

The microfabrication of the devices is described in detail in section 3.4. The enabling technology for the construction of these devices is the deep-reactive-ion etching (DRIE). Photolithography, metal deposition and multiple wafer bonding are the other critical fabrication steps. Eight identical reactor chips are produced from a single 100mm silicon wafer. Microfabrication enables the manufacture of these devices with small features and integrated electronics, batch-wise with a high degree of tolerance.

In addition to geometry, the devices described in this chapter have integrated functionality in the form of heaters and temperature sensors. Thin-film platinum heaters have been incorporated which have demonstrated heating loads up to 10 watts and chip temperatures to 400 °C. The Biot number for heat transfer was found to be much less than one (Bi<<1) indicating that the chip is nearly isothermal and temperature gradients within the reactor unlikely. The primary factor determining the thermal properties of the reactors is the packaging, not the properties of the thin-film heaters. With further advances in chip-packaging, thin-film heaters would be a viable approach to temperature control in this microreaction devices.
4. Results: The Catalytic Hydrogenation of Cyclohexene

Among gas-liquid-solid reactions practiced industrially, catalytic hydrogenations are the most common. Studies throughout the literature for mass transfer analysis in three phase systems make use of principally two model reaction systems: One is the hydrogenation of \( \alpha \)-methylstyrene to cumene, the other is the hydrogenation of cyclohexene to cyclohexane. Both reactions are considered fast at ambient conditions, so that the process is likely to be mass-transfer limited. Furthermore, since both systems have been extensively studied, the intrinsic kinetics have been established as well as the fluid properties, such as viscosity, vapor pressures, solubility of hydrogen.[79, 80] Cyclohexene was ultimately used as the model chemistry because deactivation of the catalyst could be controlled, while deactivation using the \( \alpha \)-methyl styrene chemistry could not.

4.1. Cyclohexene Hydrogenation

The hydrogenation of cyclohexene was used as the model reaction to measure the mass transfer rate. The reaction is exothermic, \( \Delta H_{\text{rxn}} = -117 \text{ kJ/mol} \),

\[
\begin{array}{c}
\text{Cyclohexene (liquid) + H}_2\text{(gas) } \rightarrow \text{ Cyclohexane (liquid)} \\
\end{array}
\]

The disproportionation of cyclohexene is a potential side reaction for this system:

\[3 \text{ Cyclohexene } \rightarrow \text{ Benzene + 2 Cyclohexane}\]
The catalyst employed was a standard platinum supported on alumina powder, where the platinum content was either 1% or 5% by weight. The metal surface area for the 1wt% Pt/Al₂O₃ catalyst was measured as 0.57 m²/g using CO chemisorption in a Micromeritics ASAP 2010 instrument. The catalyst powder was sieved and fractions of 53-75µm, 36-38µm, or <36µm were used. The amount of catalyst in the reactor was determined by the weight of the reactor before and after loading. Flow visualization was used to ensure that steady co-current flow was achieved and that the distribution of the fluid to the catalyst particles was even. This condition was especially important for the cyclohexene hydrogenation, as its high volatility could influence the reaction kinetics if the bed of catalyst particles was allowed to dry out, as in the case of the pulsing flow regime.

4.2. Intrinsic Rate Determination

To get an accurate assessment of mass transfer, the intrinsic rate for the hydrogenation of cyclohexene must be known. This intrinsic rate is the rate of reaction in the absence of all diffusional effects and mass transfer limitations and represents the highest attainable rate for a catalyst at a given set of conditions. The analysis presented here employs two approaches. The first is to take a representative value from the literature for a catalyst of similar support type and metal content. Owing to variations in catalysts, such as the method of manufacture or the nature of the porosity of the support, the variation of reaction rates from the reported values to the present analysis could be significant. Expressing the intrinsic rate as a function of the available metal surface area, rather than just the mass of the catalyst, makes the comparison less problematic. The reaction is ‘structure in-sensitive,’ so that the nature of the platinum metal surface is
insignificant. Furthermore, since the support interaction in the catalytic process is minimal for this particular reaction, reaction rates on the basis of metal surface area can be considered reliable. The second approach is to measure the intrinsic rate experimentally using a batch/slurry reactor with good mass-transfer properties. If the catalyst concentration in the slurry reactor is low enough, then the demand for hydrogen by the reaction can be tailored such that mass transfer effects are minimized. The advantage of this approach is that the exact same catalyst used in the slurry/reactor experiments, including composition as well as particle size, can be used in the microreactor studies. This eliminates any variations due to differences in the catalyst, but the drawback is that extensive studies have to be performed on the slurry-reactor to determine its own mass-transfer characteristics.

Several reaction mechanisms for cyclohexene hydrogenation have been proposed. The two presented here both reduce to a reaction that is first order in hydrogen and zero order in cyclohexene. Michel Boudart published a comprehensive investigation of intrinsic reaction kinetics of cyclohexene hydrogenation in 1978[35] and proposed that the rate for dissociative chemisorption of hydrogen on the catalyst surface was the controlling rate for the reaction:

\[
\text{Rate} = k \cdot \text{C}_2\text{H}_2
\]  

(4-1)

Their observations, as well as the observations of others, was that the concentration of the product did not affect the reaction rate, and that for reasonable concentrations of cyclohexene, the reaction was first order in hydrogen and zero order in cyclohexene. Kawakami and co-workers measured the effects on reaction rates for lower
concentrations of cyclohexene and found that the following Langmuir-Hinshelwood rate expression fit the data:

\[
\text{Rate} = \frac{k_c K_H K_{C_{\text{H}_2}} C_{\text{C}}}{(1 + \sqrt{K_H C_{\text{H}_2}})^2 (1 + K_{C_{\text{C}}} C_{\text{C}})}
\]  

(4-2)

where \( K_H \) (438 L/mol) and \( K_C \) (47.3 L/mol) are the equilibrium adsorption coefficients for hydrogen and cyclohexene respectively. This expression would suggest a mechanism of the form where the surface reaction between the dissociatively adsorbed hydrogen and the adsorbed cyclohexene is rate limiting and the adsorption of the species are considered in pseudo steady-state. For conversions of cyclohexene up to 80%, the concentration of cyclohexene, \( C_{\text{C}} \), (2 mol/L) is still much higher than that for the solubility of hydrogen, \( C_{\text{H}_2} \), (4×10⁻³ mol/L). Consequently, the rate expression in equation 4-2 reduces to the one in equation 4-1, where the reaction is first order in hydrogen.

The intrinsic rates for the hydrogenation of cyclohexene using a variety of platinum catalysts in various solvents are available in the study by Madon et al.[35] Two rate constants are defined here using standard convention: one is the surface reaction rate

\[
\text{R} \left( \frac{\text{mol}}{\text{s} \cdot \text{cm}^3} \right) = k \cdot C_{\text{H}_2}
\]

constant, \( k_{\text{sur}} \) (cm/s), the other is the volumetric rate constant, \( k \) (1/s).

\[
\text{R} \left( \frac{\text{mol}}{\text{s} \cdot \text{cm}^3} \right) = k_{\text{sur}} \cdot m \cdot A_{\text{cat}} \cdot C_{\text{H}_2}
\]
Where m is the catalyst loading (g/cm³) and A_cat is the active surface area per mass of catalyst (cm²/g). A representative value for the metal surface area is that measured for the 1wt% Pt/Al₂O₃ as 5700 cm²/g using CO chemisorption in a Micromeritics ASAP 2010 instrument. The catalyst loading is typically in the range of 0.8-1.0 g/cm³ (for example, the total weight could be 40 mg in a multichannel device with 40 µL volume).

The rate constants provided by Madon et al. are for a 2.3%Pt/SiO₂ catalyst in various solvents. The reaction rates varied by as much as 20% among the different solvents. For cyclohexene as the solvent, the activation energy, Eₐ, is 26.03 kJ/mol and the pre-exponential factor is 112 cm/s. The calculated surface reaction rate constant is,

\[ k_{sur} = 2.8 \times 10^{-3} \text{ cm/s (T=22 °C)} \]

Given a 1-2 °C variation in temperature between experiments, this value for the rate constant has a likely error of 5-10%, not including effects for the solvent or catalyst composition. For a catalyst loading of 1 g/cm³ and the surface area reported above, the intrinsic volumetric rate constant is,

\[ k = 16 \text{ s}^{-1} \]

In addition to providing rates specific to the 2.3% Pt/SiO₂, Madon et al. provide a comparison of turn over frequencies (rate of conversion per surface site) for other supports with varying levels of dispersion for the catalyst. (Dispersion defined as the fraction of metal atoms exposed at the surface to the total number of atoms). The variation in turn over frequency among the various catalysts was very small (5%) indicating that the support type and dispersion is not important to the activity of the catalyst. For example, the reported turn-over-frequency for a 0.6% Pt/γ-Al₂O₃ (dispersion=0.7) is 8.61 while that for a 2% Pt/γAl₂O₃ (dispersion=0.23) catalyst is 8.21.
Consequently, a fairly good estimate of the intrinsic rate can be made on the basis of metal surface area. So while data is not available on the intrinsic reaction rate for the exact same catalyst used in this study (5% Pt/Al₂O₃ or 1% Pt/Al₂O₃), the similarity in reaction rates on the basis of surface area supports the use of the literature value as an estimate for the intrinsic rate.

4.3. Catalyst Poisoning and Deactivation

One of the critical parameters for a heterogeneously catalyzed process is the lifetime of the catalyst. The loss of catalytic activity can be attributed to a number of factors, such as poisoning due to irreversible adsorption of impurities in the feed stock, alterations in the catalyst such as a reduction of dispersion as metal particles agglomerate at high temperatures or loss of catalyst from poor adhesion of a metal to the support. One benefit of using standard catalyst powders in a microreactor is that the chemistry and lifetime characteristics of the catalyst have already been optimized. One disadvantage of the microreactor, and of process intensification in general, is that the lifetime of the reactor becomes more sensitive to these catalyst deactivation effects. In a traditional reactor, reactor size is not at a premium, so more catalyst can be loaded than is needed for a given process. This ‘extra’ catalyst serves to buffer the losses in activity due to aging of the catalyst. In a microreactor, on the other hand, the amount of catalyst and hence the size of the reactor, must exactly match the requirements of the process since the size is engineered to operate with optimal efficiency.

For the purposes of evaluating the performance of the microreactor, it is important to have kinetics which are stable over the time of the experiment. This makes evaluating
the dependence of the reaction rate on such variables as flow rate and temperature reliable and simple to analyze. The evaluation of mass transfer rates, since they depend on the intrinsic rate, could be ascertained from initial reaction rates before deactivation occurs. When the catalysts are characterized, such as the active surface area, the calculated intrinsic rates are for initial conditions.

4.4. AMS Hydrogenation experiments

The first hydrogenation experiments were performed using α-methylstyrene as the model chemistry. The course of the experiments which attempted to elucidate the deactivation mechanism are detailed. Several potential causes for the deactivation were investigated and eliminated through various experiments.

\[
\text{AMS} + \text{H}_2 \rightarrow \text{Cumene}
\]

This reaction, like the cyclohexene hydrogenation, has been used extensively to characterize trickle-bed reactors and is a fast reaction at moderate conditions. AMS is an aggressive solvent, dissolving a wide-array of polymers and is corrosive to a number of metals. AMS is usually shipped with a polymerization inhibitor owing to its poor stability over long periods of time. Several attempts to use the AMS were made. One failure involved the corrosion of a brass component of a pressure gauge which likely deposited copper and other metals on the catalyst. The gasket material was also a concern and
several materials were used. PDMS (polydimethylsiloxane) gaskets were incompatible with the hydrophobic solvents, as the gasket swelled and failed completely. A teflon gasket (Gore Inc., Goretex gasket tape) was also used, but failed to confine the hydrophobic solvents. Viton was finally used successfully as a gasket material. Another failure involved the corrosion of the 5-port steel chuck. Prior to the current version, where the chuck is machined to accommodate the ferrules of miniature fittings, a silver-solder was used to attach tubing to the steel base plate. The AMS corroded this silver-solder causing a leak at the joint and likely metallic contamination of the catalyst. Even with a microreactor systems made entirely of compatible materials (all 316-stainless steel) and the AMS purified by removing the polymerization inhibitor, deactivation of the catalyst occurred rapidly.

The experiments shown in figures 4-1 through 4-4 use a single channel packed-bed reactor with a 5wt% palladium supported on carbon catalyst. The single channel reactor typically held 1-2 mg of catalyst. The carbon particles were rod-shaped and even though they were filtered to 50 μm, smaller particles on the order of 5-10 μm could be observed filling the channel. The conclusion is that this particular catalyst does not have the mechanical stability to retain its size integrity. In some cases, these smaller particles agglomerated in portions of the packed-bed causing the pressure drop to increase dramatically.

Figure 4-1 shows the reaction rate and conversion versus time for the hydrogenation of AMS. The catalyst was loaded into the microreactor using an ethanol slurry and 10 mL of ethanol was passed through the reactor in order to remove the water content of the catalyst. The catalyst was then ‘activated’ by passing hydrogen through
the reactor at 200 °C. Reaction was initiated by starting the liquid flow rate at 0.01 mL/min of pure AMS (still retaining the polymerization inhibitor). The reaction rate then continued to decrease over the course of several hours until no activity was observed. At this point, the activation procedure was repeated, but no gains in activity were made. Figure 4-2 shows the reaction rate profile for substrate that has been purified (inhibitor removed), but no activation procedure. The reaction rate increases initially (presumably from the lack of activation) and then decays rapidly. This eliminates the inhibitor as the cause of the deactivation. The temperature was gradually increased in increments to recover the activity. At 110 °C, and after most of the activity had been lost, pure AMS only was passed through the reactor for 5 hours in an attempt to dissolve any oligimers or polymerized species that may be blocking the pores of the catalyst. This also failed to recover the activity.

**Figure 4-1.** Hydrogenation of AMS in a single channel microreactor loaded with 50 μm catalyst particles. A severe loss in reaction rate is observed over the course of the experiment.
In the last experiment, purified AMS was diluted in heptane to 10 wt% and used as a substrate. Figure 4-3 compares the rate of deactivation with the concentration of AMS in the substrate. As a result of diluting the AMS, the deactivation rate was decreased. As seen in figure 4-4, when the reaction rate is compared to the amount of AMS fed to the reactor (which is independent of concentration), rather than time the rate of deactivation is similar. The conclusion drawn is that the deactivation of the catalyst is due to some component in the AMS or the AMS itself poisoning the catalyst.

![Graph showing reaction rate vs. time with conversion percentages]

**Figure 4-2.** AMS hydrogenation in a single channel microreactor. Deactivation continues with an increase in temperature. Flowing AMS only does not recover the activity.
Deactivation during AMS hydrogenation is mentioned only briefly in the literature[32]. Watson and co-workers discuss and provide evidence for, the formation of oligomeric species from the AMS. Self-polymerization is known for AMS, hence the polymerization inhibitor. The oligomeric species have a low volatility, as well as a low solubility, so that diffusion within the pores of the catalyst becomes hindered.

![Graph]

**Figure 4-3.** AMS Hydrogenation in a single channel microreactor. When AMS is diluted to 10% by weight in ethanol, the rate of deactivation is decreased indicating that the source for deactivation is some component of the AMS.
Figure 4-4. Deactivation of the rate of hydrogenation normalized for the amount of AMS fed to the reactor.
4.5. Cyclohexene Deactivation and Purification Procedures

Mechanisms for the deactivation of catalysts used for cyclohexene hydrogenation are also reported.[81, 82] Procedures for purifying cyclohexene and preventing deactivation are more readily available in the literature than for the AMS hydrogenation. Two mechanisms predominate: one is the build up of carbonaceous residues on the catalyst, the other is the formation of a hydroperoxide from the cyclohexene which poisons the noble-metal catalyst. A stable cyclohexene epoxide is reported to form when cyclohexene come in contact with air.[80] The hydroperoxide irreversibly adsorbs to the catalyst and reduces the surface sites available for reaction. Madon et al. report a procedure for purifying the cyclohexene to remove these and other contaminating species.[35] Their method calls for passing the cyclohexene through alumina powder and storing under helium. Watson et al report a similar procedure. Somorjai report a procedure whereby the cyclohexene is refluxed in the presence of CaH₂ and stored under argon. [80]

To compare the effects of a given purification procedure, cyclohexene was first used as received from Aldrich (with 0.01% BHT stabilizer). Figure 4-5 shows the reaction rate for the hydrogenation performed in a single-channel reactor using a 5wt% Pt/Al₂O₃ catalyst. This alumina catalyst was found to have superior mechanical properties relative to the carbon catalysts. For this first experiment, without any treatment of the substrate, the activity decreased as before.
Figure 4-5. Cyclohexene hydrogenation in a single channel reactor. No purification leads to a loss of activity similar to the AMS experiments.

4.5.1. Cyclohexene Purification

In a nitrogen glove box, cyclohexene was mixed with alumina powder overnight. The cyclohexene:alumina weight ratio was 10:1. The alumina powder is the same activated $\gamma$-alumina powder sold by Aldrich as a polymerization inhibitor remover. The advantage of using this alumina powder is that it has a high surface area, it is in the form of a finely divided powder, and is shipped and stored under nitrogen without contact to air. After mixing overnight, the cyclohexene was dissolved in ethanol (also stored in the nitrogen glove box) and transferred using a gas-tight glass syringe with a teflon plunger and valve. The catalyst was purged with hydrogen for 1 hour at room temperature, ensuring that most of the air in the system was removed.
Using these procedures, stable reaction kinetics were obtained. Figure 4-6 shows the time profile for the reaction rate using procedures outlined above. The reaction rate initially declines 28% from 4.6×10⁻⁶ mol/min to 3.3 mol/min, but remains steady over the course of two hours, deviating by less than 1%. This initial decay in the reaction rate is consistent with cycloalkene hydrogenations.[81]

![Graph showing reaction rate over time](image)

**Figure 4-6.** Cyclohexene hydrogenation in a single channel microreactor. With proper purification, the rate remains steady after an initial loss of activity.

Others report similar initial decay followed by steady reaction rate, attributing the decay to an initial deposit of carbonaceous material on the catalyst. To further verify experimental procedures, Figure 4-7 shows the reaction rate on the second day of experiments using the same catalyst. After running the reaction for 10 hours at varying conditions, the reactor and catalyst was left overnight sealed from exposure to air. Fresh
substrate was used and the reaction rate remained constant (deviating by only 2%) for almost two hours. The reaction rate declined slightly from the end of the previous day by approximately 10%. The gradual decline in reaction rate, as observed by the difference in reaction rate from Figure 4-6 to Figure 4-7 prevents the extensive re-use of the catalyst for the purposes of kinetics investigations. For all of the studies in this thesis, fresh catalyst and substrate was used each day.

![Graph showing reaction rate over time](image)

**Figure 4-7.** Cyclohexene hydrogenation. Reaction rate remains steady for the second day of using the same catalyst and using a new substrate.
4.6. Reaction Results

Conversions near 10% at liquid flow rates near 0.1 mL/min yielded observed reaction rates ranging from $0.9 \times 10^{-3}$ to $1.4 \times 10^{-3}$ mol/(min. g cat.), depending on the flow rates of the gas and liquid streams. For comparison, the intrinsic reaction rate was estimated as $3.4 \times 10^{-3}$ mol/(min. g cat.) from reported literature values and the measured metal surface area. In general, the reaction rate (corrected for differences in pressure) was observed to increase as the flow rate of either the gas or liquid was increased. This suggests that mass transfer limitations play a role in the observed kinetics. In traditional laboratory reactors, mass transfer coefficients vary with the liquid Reynolds number even when the Reynolds number is small (typical Reynolds number for these experiments is $Re = 0.05$).[83] The purity of the cyclohexene also affected the catalyst activity. Without proper purification, the activity was observed to decrease significantly over the course of several hours. Purification procedures were similar to those reported elsewhere.[32] For all of the data reported, the kinetics were averaged over a time period where the activity of the catalyst deviated by no more than 5% from the initial steady reaction rate.

4.6.1. Activation Energy for the Cyclohexene Hydrogenation

With stable reaction kinetics, the influence of various parameters upon reaction rate could be investigated without having to load a new catalyst for every experiment. This also helped to eliminate any variations in reaction rate due to the amount of catalyst loaded or the pre-treatment of the catalyst for each experiment. Figure 4-8 shows the results for a single channel reactor loaded and the increase in reaction rate with increases
in temperature. Initially, the reaction rate showed steady behavior at $T = 30 \, ^\circ\text{C}$, and then once the temperature was stabilized at the various set-points, three data points were collected for each temperature. The conditions were identical for each temperature (Liquid Flow Rate = 10 mg/min., Gas Flow Rate = 10 sccm). Table 4-1 lists the average reaction rate along with the standard deviation and the reactor conditions. An experimental activation energy was obtained from this data as seen in the Arrhenius plot in Figure 4-9. Although the linear regression was excellent ($r^2=0.999$), a slight standard deviation in the temperature (~5%) causes for large errors in determining the activation energy. From the data in Table 4-1, the activation energy, $E_A$ is calculated to be $18.5 \pm 5$ kJ/mol. This value can be compared with the activation energy reported by Madon et al, $E_A=25 \pm 2$ kJ/mol. Even considering the error, the activation energy observed here is lower and is likely due to a mass transfer influence. [60]

**Table 4-1.** Cyclohexene reaction rate versus temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Average Reaction Rate (mol/minute)</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.1 +/- 0.9</td>
<td>2.13×10^{-6}</td>
<td>2.7%</td>
</tr>
<tr>
<td>40.6 +/- 0.6</td>
<td>2.75×10^{-6}</td>
<td>2.0%</td>
</tr>
<tr>
<td>50.3 +/- 3.1</td>
<td>3.36×10^{-6}</td>
<td>2.0%</td>
</tr>
</tbody>
</table>
Figure 4-8. Cyclohexene hydrogenation rate versus temperature.

Figure 4-9. Arrhenius plot for the cyclohexene hydrogenation.
4.6.2. Reaction Results: Single Channel Reactor Hydrogenation

Table 4-2 summarizes data collected for the hydrogenation of cyclohexene in a single channel reactor for constant temperature. The catalyst weight loaded was 3.3mg and all of the data were collected at 22 °C. The procedure for collecting the rate data involved stabilizing the flows for a given set of flow rate conditions and collecting reaction results over the course of an hour (3-4 points). The reaction rate was determined by multiplying the conversion as determined from the GC analysis with the liquid flow rate measured at each point.

Table 4-2. Various Reaction Results for Hydrogenation in a Single Channel Reactor

<table>
<thead>
<tr>
<th>Data Point</th>
<th>Substrate</th>
<th>Catalyst</th>
<th>Liquid Flow Rate (mg/min.)</th>
<th>H₂ Flow Rate (SCCM)</th>
<th>Pressure (PSIG)</th>
<th>Reaction Rate mol/min./mg</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100% Cyclohexene</td>
<td>50-71μm 5wt% Pt/Al₂O₃</td>
<td>13.3</td>
<td>4</td>
<td>3.6</td>
<td>5.00 x 10⁻⁷</td>
<td>8%</td>
</tr>
<tr>
<td>2</td>
<td>“</td>
<td>“</td>
<td>30.3</td>
<td>4</td>
<td>4.4</td>
<td>2.80 x 10⁻⁷</td>
<td>19%</td>
</tr>
<tr>
<td>3</td>
<td>“</td>
<td>“</td>
<td>24.7</td>
<td>12</td>
<td>8.1</td>
<td>3.10 x 10⁻⁷</td>
<td>3%</td>
</tr>
<tr>
<td>4</td>
<td>“</td>
<td>“</td>
<td>6.8</td>
<td>1.2</td>
<td>1.5</td>
<td>4.50 x 10⁻⁷</td>
<td>9%</td>
</tr>
<tr>
<td>5</td>
<td>“</td>
<td>“</td>
<td>6.7</td>
<td>4</td>
<td>2.9</td>
<td>4.70 x 10⁻⁷</td>
<td>11%</td>
</tr>
<tr>
<td>7</td>
<td>“</td>
<td>36-38 μm 5wt% Pt/Al₂O₃</td>
<td>12</td>
<td>20</td>
<td>12.5</td>
<td>1.20 x 10⁻⁶</td>
<td>13%</td>
</tr>
<tr>
<td>8</td>
<td>“</td>
<td>“</td>
<td>13.5</td>
<td>10</td>
<td>7.3</td>
<td>9.70 x 10⁻⁷</td>
<td>5%</td>
</tr>
</tbody>
</table>

A number of observations can be made with this data set. First, it appears from data points 1,2 and 5 that increasing the liquid flow rate, for a constant gas flow rate, has a little effect, or slightly decreasing effect, on the reaction rate. From data points 2 and 3,
it can be observed that increasing the gas flow rate, for a given liquid flow rate, has little effect on the reaction rate.

The effect of particle size can be more clearly observed in data points 7-8. The reaction rate is higher for the smaller, more discrete particle size. Comparing data points 8 and 3, the reaction rate is 3X higher, even though the pressure is nearly the same. (The pressure will determine the saturated solubility of hydrogen, and hence the reaction rate) The effect on the pressure drop by the particle size is also observed for these points given that the liquid flow rate is higher for the larger particle size.

Two conclusions can be drawn from this data set. First, the flow conditions have less of an influence on the observed reaction rate as compared to the influence of the particle size of the catalyst. The particle size effect could be caused by two mechanisms. One mechanism is a diffusional limitation in the pores of the catalyst which would be reduced for smaller particle sizes. This is unlikely to cause the reaction rate to increase by a factor of three. In the section on mass transfer analysis, internal diffusion is estimated to limit the reaction by only 20%. The most likely mechanism is the distribution of the two phases throughout the packed bed. With the smaller particle sizes, the bed is more likely to be uniform, and the pressure drop slightly higher such that the phases get distributed throughout the bed of particles. In essence, for the smaller particles, the bed is packed more uniformly and the utilization of the catalyst is greater.

The second conclusion is that pressure drop for the two-phase flow follows an expected linear trend for increasing flow rates of the gas and liquid phases. The pressure drop is more strongly dependant on the flow rate of the gas than that of the liquid, according to data points 1-6.
4.6.3. Reaction Results: Hydrogenation in a Multichannel Reactor

Using the same 5wt% Pt/Al2O3 catalyst as in the single channel reactor experiments, cyclohexene hydrogenation was performed in a ten-channel device. Table 4-3 summarizes the results for the various conditions employed.

Table 4-3. Various Reaction Results for Hydrogenation in a Multi Channel Reactor

<table>
<thead>
<tr>
<th>Data Point</th>
<th>Substrate</th>
<th>Catalyst</th>
<th>Liquid Flow Rate (mg/min.)</th>
<th>H2 Flow Rate (SCCM)</th>
<th>Pressure (PSIG)</th>
<th>Reaction Rate mol/min./mg</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100% Cyclohexene</td>
<td>38-51µm 5wt% Pt/Al2O3</td>
<td>15.5</td>
<td>5.0</td>
<td>0</td>
<td>8.6 x 10^-7</td>
<td>4%</td>
</tr>
<tr>
<td>2</td>
<td>&quot;</td>
<td>&quot;</td>
<td>153</td>
<td>5.0</td>
<td>2.0</td>
<td>1.4 x 10^-6</td>
<td>1%</td>
</tr>
<tr>
<td>3</td>
<td>&quot;</td>
<td>&quot;</td>
<td>71.2</td>
<td>5.0</td>
<td>4.0</td>
<td>1.1 x 10^-6</td>
<td>7%</td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>&quot;</td>
<td>78.5</td>
<td>3.2</td>
<td>4.2</td>
<td>9.7 x 10^-7</td>
<td>5%</td>
</tr>
<tr>
<td>5</td>
<td>&quot;</td>
<td>&quot;</td>
<td>72.2</td>
<td>6.6</td>
<td>5.7</td>
<td>1.4 x 10^-6</td>
<td>3%</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>&quot;</td>
<td>16.0</td>
<td>2.0</td>
<td>0</td>
<td>9.2 x 10^-7</td>
<td>7%</td>
</tr>
<tr>
<td>7</td>
<td>&quot;</td>
<td>&quot;</td>
<td>54.6</td>
<td>10</td>
<td>4.2</td>
<td>1.4 x 10^-6</td>
<td>10%</td>
</tr>
</tbody>
</table>

Figures 4-10 and 4-11 plot these data points to illustrate the influence of flow rates on the reaction rates. The velocity has been determined by dividing the volumetric flow rate by the cross-sectional area of the channels. In both cases, the reaction rate increases with increasing velocity of either of the gas phase or the liquid phase.

This increase in rate with velocity is consistent with other results in the literature, whereby an increase in velocity improved the mass transfer coefficient, and consequently the rate of the reaction. The effect here could be convoluted: increasing the flow rates serve to better distribute the fluids among the ten channels and consequently utilization of the catalyst is higher.
**Figure 4-10.** Reaction rate dependence on liquid velocity for the cyclohexene hydrogenation in a multichannel reactor. The increase in activity is due to a combination of improved mass transfer and better distribution of the reagents to the catalysts.

**Figure 4-11.** Reaction Rate dependence on gas velocity for the cyclohexene hydrogenation in a multichannel reactor.

Figure 4-12 compares the rate data in the multi-channel reactor with the data in the single channel reactor. Two observations can be made. First, is that the reaction rate is consistently higher in the multichannel reactor compared with a single channel reactor. Second, that increasing the liquid velocity increases the rate in the multichannel reactor,
where liquid velocity has little to no influence on the reaction rate in the single channel reactor. This second point would indicate that the distribution of the fluids in the multichannel reactor is the predominate mechanism whereby the reaction rate is improved. The fact that the rate per mass of catalyst is higher in the multichannel reactor indicates that the fluids are distributed evenly to some degree, i.e. there is no gross flow maldistribution where 20-30% of the catalyst is unused. The productivity of the multichannel reactor is consistent with the fact there is nearly 10X the amount of catalyst.

For data point 7 of table 4-3 (multichannel), the conversion is 9% at 55mg/min, or 5 mg/min of product, while for data point 7 of table 4-2 (single channel), the conversion is at 2.3% at 12 mg/min, or a production rate of 0.3 mg/min.

**Figure 4-12.** Comparison of reaction rates for the cyclohexene hydrogenation in the single channel reactor and the multichannel reactor.
4.6.4. 1% Pt/Al2O3 Reaction Results

The results of Figure 4-12 indicate that reaction rates improved with smaller particle size. The effect could be the result of a number of factors. One is the liquid diffusion mass transfer, one is the gas-liquid mass transfer, the other is the catalyst utilization, or distribution efficiency to the catalyst. To see if reaction rates could be improved further, size fractions for the alumina catalyst were used that consisted of particles smaller than 36 µm. The capabilities of traditional sieve equipment limit the size of filtration to 36 µm. The result is that the size distribution could in effect, be very large. The pressure drop was expected to increase as a result of the smaller particles, but the expected tradeoff would be in terms of better distribution of the fluids and higher reaction rate. In Section 4-3, the results of the improved flow distribution are demonstrated. Table 4-4 summarizes the results for the 1% Pt / Al2O3 catalyst in the microreactor.

<table>
<thead>
<tr>
<th>Data Point</th>
<th>Substrate</th>
<th>Catalyst</th>
<th>Liquid Flow Rate (mg/min.)</th>
<th>H2 Flow Rate (SCCM)</th>
<th>Pressure (PSIG)</th>
<th>Reaction Rate mol/min./mg</th>
<th>Std. Dev.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100% Cyclohexene &lt;36µm 1wt% Pt/Al2O3</td>
<td>75</td>
<td>10</td>
<td>10.1</td>
<td>2.0 ×10⁶</td>
<td>6%</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>&quot;</td>
<td>&quot;</td>
<td>15</td>
<td>3.2</td>
<td>4.2</td>
<td>9.0 ×10⁷</td>
<td>7%</td>
</tr>
</tbody>
</table>

Table 4-4. Various Reaction Results for Hydrogenation in a Multi Channel Reactor
4.7. Batch Experiments

Batch experiments were performed as an alternative means to arrive at an intrinsic rate constant and to check the applicability of the rate data provided in the literature. The experimental set up and procedure are briefly described. A 250 mL, three neck flask was fitted with a thermometer, a gas inlet line, and a magnetic stirrer. The ports on the flask were sealed with a neoprene rubber septum. In a nitrogen glove box, the flask was charged with a certain amount of cyclohexene and catalyst, such that the catalyst to substrate ratio was low (~1:100). Once the flask was sealed, it was transferred from the glove box to a fume hood and connected to the hydrogen gas inlet line. Prior to the commencement of stirring, the gas volume above the substrate in flask was purged three times with hydrogen. Once the flask was charged with hydrogen, stirring was initiated and this was taken as time zero for the reaction. After certain intervals of time, samples (~200μL) were withdrawn from the flask and analyzed using GC-MS.

Figure 4-13 plots the reaction results in the form of conversion versus time. Conversion was determined on the basis of the relative peak areas for the total ion chromatograms. If $A_1$ and $A_2$ are the integrated peak areas for cyclohexene and cyclohexane respectively, then the conversion, $X$ is

$$X = \frac{A_2}{A_1 + A_2}$$

This assumes that the substrate is only converted to a single product and that the peak area is linearly proportional to the concentration of the species. Both assumptions were verified. No other products for the reaction were detected and the peak response was calibrated with concentration and found to have a linear dependence.
Figure 4-13. Batch/Slurry reactor results for cyclohexene hydrogenation. 10 mL of pure cyclohexene, 54 mg of 1wt%Pt/Al2O3 sieved to <36 μm, T=22 °C.

The conditions of the reaction were the following: 10 mL of pure cyclohexene, 54 mg of 1wt%Pt/Al2O3 sieved to <36 μm, T=22 °C. Figure 4-14 plots the data as a reaction rate versus time. The reaction rate at each data point was calculated using the total conversion to that point and dividing by the total time elapsed. The reaction rate increased over time, approaching a steady value for the last three points of 1.25×10⁻⁷ mol/s/cm³ +/- 3%, or 1.4 mol/(min mg cat). The initial increase in reaction rate is presumably due to some initial activation of the catalyst. Using a solubility of hydrogen, $C_{\text{sat}}(H_2) = 3.6×10^{-6}$ mol/cm³, a surface area of the catalyst (5700 cm²/g), and a catalyst loading of $5.4×10^{-3}$ g/mL, the intrinsic rate constant would be,

$$k_{\text{surf}} = 1.13×10^{-3} \text{ cm/s}$$
This value is only 40% of the rate constant predicted by the literature values above. This would suggest that even the batch reaction has a certain mass-transfer limitation associated with it.

Figure 4-14. Reaction rate results for cyclohexene hydrogenation in a batch / slurry reactor using the data from Figure 4-13.

The gradual increase in reaction rate to the steady value of $1.25 \times 10^{-7}$ is not due to absorption of the hydrogen into the liquid. There is indeed an induction period during which the hydrogen absorbs into the liquid. But if that time were on the same scale as the induction for the reaction rate (~10 minutes), then the $K_a$, or the characteristic time scale would have to be on the order 0.001 s⁻¹ (1/10 minutes). If the $K_a$ were this low, then the maximum steady state reaction rate ($R_{\text{max}} = K_a \cdot C_{\text{sat H2}}$) would have to be $3.6 \times 10^{-9}$ mol/s/cm³. The steady state reaction rate is in fact much higher than this. A possible explanation for the induction period is the gradual activation of the catalyst due to
The catalyst may not be fully reduced at the start of the reaction and during the course of the experiment more surface sites may become available for reaction.

The same procedures were used to determine the reaction rate for the 5wt% Pt/Al2O3 catalyst. For a catalyst size of 53-71 μm, the reaction rate, using the batch reactor, was measured as 2.6×10⁻⁶ mol/(min mg cat).

4.8. Reaction Results Summary

![Calculated Overall Reaction Rates versus Mass Transfer Coefficients](image)

**Figure 4-15.** Expected reaction rates for a range of mass transfer rates using the intrinsic reaction rate for the cyclohexene hydrogenation. Reported values of Kla would produce reaction rates several orders of magnitude lower than the rates observed in the microreactor.
4.9. Microfluidics Results


In traditional laboratory reactors involving multiple phases, the behavior of the multiphase fluid flow can have a substantial effect on the performance of the reactor. Various flow regimes can exist ranging from bubbling flow to pulsing flow and are traditionally characterized by a flow regime map.[84] Flow regimes in the microfabricated reactor have been characterized visually using optical microscopy. Figures 4-16 and 4-17 illustrate the nature of the gas-liquid flow for various flow rates of the hydrogen/organic liquid system. For low liquid and gas velocities, bubbles form at the distributor and are carried by the liquid to the packed-bed. When the flow rates become sufficiently high, the liquid wets the walls of the channel prior to the packed bed and a stable gas-liquid interface develops. For a given liquid flow rate, as the gas flow rate increases, the gas-liquid interface near the distributor (see Figure 4-17) begins to oscillate in a pulsing fashion. With a continued increase in the gas flow rate, the relative phases become more segregated, resulting in a periodic "drying-out" of the packed bed. Figure 4-19 is a photomicrograph comparing the bed packing between a liquid pulse and a gas pulse. Figure 4-18 compares the transition point from steady flow to pulsing flow with a regime map originally proposed by Charpentier in 1975. [84]

Though it has been shown that operating in a pulsing flow regime can improve performance, it complicates the interpretation of mass transfer and kinetic data.[85] Therefore, for all of the experimental kinetic data reported here, the reactor was operated
in the steady co-current flow regime. In traditional packed-bed reactors, pulsing flow can cause major pressure fluctuations that can cause mechanical damage to the packing.

Figure 4-16. Fluid flow regime characterization in single channel reactor.
(A) "Bubble flow", Liquid flow rate = 10 μL/min, gas flow rate = 1 sccm.
(B) "Steady" Co-current Flow, liquid flow rate = 10 μL/min, gas flow rate = 5 sccm.
Figure 4-17. Photomicrograph of pulsing flow.

Single channel reactor, liquid flow rate = 10 µL/min, gas flow rate = 10sccm. Time sequence illustrates the oscillatory behavior of the gas-liquid interface near the inlets.
Figure 4-18. Flow transition point versus superficial mass velocities: microreactor compared with published laboratory reactor.
- Microreactor Cyclohexene/H₂
- Charpentier Flow Map

Figure 4-19. Drying out of the catalyst bed due to a gas pulse.
A) Packed-bed with both gas and liquid flow.
B) Drying out of the porous catalyst in the packed bed. As the pulse of gas travels through the bed, the liquid evaporates.
4.9.2. Flow Distribution

One of the traditional problems in reactor design, particularly for multiphase reactions, is one of uniform distribution of reagents throughout the reactor volume. Since each of the two reactants are present as different phases, both phases must access the catalytic sites within the porous particles. Capillary forces tend to cause the liquid to wet the porous catalyst. As a result, the gas phase reagent must diffuse through the liquid film surrounding the particle. In a traditional trickle-bed reactor, the catalysts are in the form of cylindrical pellets 4-10 mm in diameter. The pellets fill the tubular reactor in a random arrangement. So in addition to the mesoscale issue of gas and liquid reagents diffusing to the catalytic sites, there is an issue of macro scale distribution. Gas and liquid phases must be uniformly distributed at the reactor inlet, and the packed-bed itself must promote a uniform co-current flow through the reactor volume. Traditional equipment for trickle-bed reactors employ a liquid spray at the top of the reactor to distribute the liquid reactant within the gas phase. But as the diameter of the overall reactor increases, either as a result of scale-up or in the reactor geometry proposed in chapter 2, it becomes much more difficult to manifold the distribution of the two reagents across the large inlet area.

Ideally, each pellet would be wetted with the liquid reagent and surrounded by the gas phase. In reality, flow patterns develop in which the liquid wets clusters or bundles of pellets and the gas phase has a much longer path of diffusion to the pellets in the center of the cluster. In the reverse case, gas-phase flow may predominate along certain channels throughout the packed-bed resulting in collections of catalytic pellets which are completely dry and absent of any liquid phase. In these dry zones, the only reaction is
that in the vapor phase which is likely to be much slower owing to the limited volatility of reagents used in three-phase processes. These macroscale flow maldistributions results from variations in the packing density. Other effects for industrial reactors include the physical attrition of catalyst pellets to form particle 'fines' which block the flow and increase the pressure drop.

Poor flow distribution is a traditional engineering challenge for packed-bed reactors. In the packed-bed microreactors of this thesis, similar issues associated with flow distribution were observed. The effect was more pronounced in the multichannel design. The ten parallel channels operate independently: there is no transfer of flow between adjacent channels. The consequence of this is that if there is an irregularity in the packing at any point along the length, then flow gets diverted at the start of the reaction channel, rather than at the start of the irregularity. The packing irregularity could be a higher frequency in voids between adjacent particles, in which case the pressure drop would be reduced and attract flow. The opposite effect could be one where a cluster of smaller particles pack tightly, thus repelling flow to the other channels. The flow distribution in this microreactor depends upon the arrangement of the packing because the packing is the most significant pressure drop in the system. Figure 4-20 illustrates some of these effects for liquid flow rates near 0.1 ml/min. and gas flow rates near 20 SCCM.
**Figure 4-20.** Flow maldistribution in the packed beds.

A) Gas channeling in beds with 50-70 μm particles.
B) Channels now filled with 36-38 μm particles. Because of uneven loading or packing density, the liquid completely bypasses several of the channels.

In figure 4-20A, gas and liquid phases are distributed among the inlet manifold, but are diverted once reaching the start of the reaction channels. As can be seen in the figure, a reaction channel has formed a rivulet of gas, effectively causing the gas to bypass most of the catalytic particles. In the channel immediately below, flow is entirely liquid. No gas flow penetrates into the packing, and the result is that the reaction is limited by the absence of the gas reactant. The packing in figure 4-20A is of the particle
size 51-73 \( \mu m \) Assuming that the average particle size is 60 \( \mu m \), then the ratio of channel diameter to particle size is 10:1 across the width and 5:1 across the depth. The general consensus in the reaction engineering literature is that this ratio should be at least 10:1 in order for a uniform arrangement of the particles to develop. To accomplish this, smaller particles with a tighter size distribution (36-38\( \mu m \)) were loaded into the reactor and the flow behavior analyzed. The result was that the mode of catalyst loading had a more severe impact on the flow distribution. Figure 4-20B shows the two-phase flow in a multichannel reactor loaded with 36-38 \( \mu m \) alumina particles. The flow in the top two channels is entirely liquid, while that in the bottom channels of the picture are filled entirely with gas. The intermediate channel demonstrates some flow of both phases, suggesting that the packing density, or pressure drop steadily varies across the channels. The pressure drop is the least near the top, since the higher viscosity liquid will have a greater resistance to flow and divert to the channels with the lowest resistance. The variation in packing density across the channels is due to loading of the catalyst into the channels sequentially, rather than simultaneously. The lower channels finished loading first, and gradually the channels were filled from bottom to top. The reasons the channels loaded in this fashion is that the bottom-most catalyst inlet port was used to deliver the particle slurry, while the top catalyst inlet port was used only to receive excess particle flow.

When both catalyst inlet ports were used to deliver the particle slurry, in addition to a cross flow provided by the gas and liquid inlets, the particles filled the channels simultaneously, thus allowing for a more even packing distribution among the ten channels. The effects can be observed in Figure 4-21. In Figure 4-21A, the two phases
are evenly distributed. The channel at the bottom still contains liquid stagnation regions, but for most of the device the flow is much more uniform. Figure 4-21B, indicates the flow at the exit. The ports immediately after the particle filter were used to confirm two-phase flow in each channel, as the gas-liquid interface could be easily observed.

**Figure 4-21.** Even distribution of multiphase flow in a packed-bed. 36-38 μm catalyst particles. A) Entrance. B) Exit streams illustrating co-current flow at the outlets.
4.9.3. Two-Phase Flow Pressure Drop

The pressure drop in the ten parallel channel reactor followed the expected trend based on equation (1): for similar flow rates, the pressure was reduced by a factor of ten. The experimental two-phase pressure drop is plotted in Figure 4-22 for the single-channel reactor. The gas flow rate is constant at 4SCCM and the liquid flow rate varies. The expected pressure drop on the basis of the liquid flow alone and using the Ergun equation is plotted with the experimental data. The two-phase pressure drop is a factor of 2-3 times higher than that predicted for single phase flow alone. As expected, the gas flow is occupying a portion of the void volume and the effective volume available for the liquid is reduced.

![Graph showing two-phase pressure drop](image)

**Figure 4-22.** Two-phase pressure drop in a single channel reactor. The addition of gas flow at 4scm increases the pressure drop.
4.10. Summary

In this chapter, the catalytic hydrogenation of cyclohexene to cyclohexane was used as a model multiphase chemical reaction to characterize the performance of the microreactors. The first step was to determine the intrinsic kinetics, that is the reaction rate in the absence of any mass transfer or diffusional limitations. This was accomplished by extrapolating rate data from the literature as well as performing batch, slurry reactor experiments. The second step was to achieve stable reaction kinetics so as to determine the influence of various parameters, such as flow rates and temperature, on the reaction rate. Poisoning and deactivation of the catalyst was prevented by employing careful preparation procedures for the catalyst and substrate. Having determined the intrinsic rate and maintaining stable reaction kinetics, reaction rate data was collected in the single channel reactor and in the multichannel reactor for various flow rates, temperatures, and catalysts.

Performing the multiphase reaction also allowed the characterization of the fluid flow in the microreactors. The two-phase flow in the micro packed-beds varied depending upon the relative rates of the gas and liquid streams. Various flow regimes were observed, such as bubbling flow, steady flow, and pulsing flow, and were found to be consistent with flow regimes observed in conventional reactors. The flow distribution presented a challenge in the multichannel reactor because the fluid flow was found to be highly sensitive to the loading density of the catalyst for each of the ten channels. Nevertheless, flow conditions were achieved such that the reaction performance in the microreactor could be quantitatively assessed and compared with conventional reactor design.
5. Mass Transfer and Reactor Analysis

The reaction results from chapter 4 indicate that the reaction rates in the microreactors are dependant upon the flow rates of the gas and liquid phases and the particle size of the catalyst, even when the same reaction conditions are employed (temperature, pressure, catalyst). This is consistent with a wide range of multiphase reaction processes where the reaction rate is inhibited by mass transport effects. When the observed reaction rate for a given reactor is less than expected based on the intrinsic kinetics of the chemical reaction, a physical transport process is often the culprit. Any number of approaches could be used to describe the influence of the transport upon the reaction process, but the model used here is a thin-film approach consistent with traditional chemical reaction engineering analysis. This allows a meaningful comparison with reactor analyses in the literature, even if the physical description is not always exact.

A number of factors can have a deleterious effect upon the reaction rate, including flow distribution (catalyst wetting efficiency), and mass transport of a reactant species to the catalytic site. For fast reactions, the gas-phase reactant can become depleted in the liquid-phase and the rate of gas absorption into the liquid or diffusion within the liquid to the catalyst can become rate limiting. In the thin-film approach to mass transport, the rate of material transport is linearly related to a concentration gradient by a mass transfer coefficient, $k_L$. The higher the mass transfer coefficient, the higher the rate of mass transfer for a given reactor configuration.

A number of assumptions are required in order to apply this thin-film approach. First, is that the mass transfer coefficient is the same everywhere in the reactor. Provided that the catalyst loading density is the same, the catalyst particle size is the same, and that
the reactor is isothermal, this is not a difficult assumption to make. The more difficult assumption is that the reaction conditions are at steady state. This assumes that the rate of gas absorption into the liquid is balanced by the rate at which it is consumed by the reaction. This assumption is addressed in the next section.

After addressing these assumptions, this chapter provides a justification for the use of a heterogeneous reaction to assess mass transfer and then a justification for using co-current gas-liquid flow for the reactors. After which, the model for the mass transfer of the gas-liquid-solid reaction is derived. Using this model, the mass transfer coefficient, $K_L\alpha$ is calculated based on the reaction results of the previous chapter. In this way, a quantitative assessment of the microreactor’s performance is provided on the basis of experimental evidence.

5.1. Is the steady-state assumption for gas absorption valid?

For most of the mass transfer analysis, steady state operation is assumed. Given that the design of the reactor calls for a short, wide reactor geometry, entrance effects could become significant. To determine if this is the case for absorption of hydrogen into the liquid, the time required to saturate the liquid for a given mass transfer is calculated. The time to reach saturation is the inverse of the $K_L\alpha$. If $K_L\alpha$ is 1 s$^{-1}$ (lower bound for values observed in the microreactor) and the solubility, $C_{sat}$, is $3.6 \times 10^{-6}$ mol/cm$^3$, then the rate of absorption is $3.6 \times 10^{-6}$ mol/cm$^3$/s and the time to reach $C_{sat}$ is 1 second. For a liquid flow rate of 0.1 mL/min, a reactor volume of 0.04 mL, the residence time, $\tau$, is 24 seconds. Hence, the time the reactants spend in the reactor is much longer than the time
required to reach saturation. This could be expressed as a Damkohler number for mass transfer:

$$Da = k_i a \cdot \tau$$  \hspace{1cm} (5-1)

For large values of Da (Da > 1) the residence time is sufficiently large that gas-liquid absorption can be considered steady state. The minimum value of this Damkohler number for the microreactors in this work is Da ≥ 24.

5.2. Why use a heterogeneously catalyzed reaction to assess mass transfer?

A number of different approaches are available for ascertaining the mass transfer limitations in a multiphase packed-bed reactor. For determining gas-liquid absorption mass transfer, a variety of experiments are described in the literature and are classified as either physical or chemical methods. The major drawback to these methods for the microreaction systems is analysis. With the heterogeneous catalyzed reaction, the reaction ceases to occur once the reagents have left the reactor. With these homogeneous chemical reactions, where conversion takes place within the liquid phase once the two phases have contacted, the reaction proceeds even after the reagents have left the reactor. The volume space in the packaging between the reactor and the collection vial is sufficiently large that the two phases will be in contact for a time which exceeds that within the microreactor. One way to overcome this would be to integrate sensing directly into the reactor at the exit point of the reactor. Another way would be to incorporate
some means for quenching the reaction, either by temperature or some other chemical reaction.

5.3. Why is Co-Current Flow Necessary?

Different modes of operation could be envisioned for reacting the liquid substrate with the hydrogen gas. One mode would be to pre-mix the liquid and gas until the liquid was saturated with the gas and then react the mixture over the catalyst. To understand why this is not possible and why co-current flow of the hydrogen is necessary, consider the following argument. The saturated solubility of hydrogen in cyclohexene, for example, is $3.6 \times 10^{-6}$ mol/cm$^3$. Given the molecular weight (82 g/mol) and density (0.8 g/cm$^3$) the concentration of pure cyclohexene ($1 \times 10^{-2}$ mol/cm$^3$) is 10,000 times larger than the concentration of hydrogen. Even at elevated pressures, the concentration of hydrogen dissolved and available for reaction is extremely low. At even the slightest amount of conversion, all of the hydrogen will be consumed. As the hydrogen is consumed from the liquid media, it must be continually replenished.
5.4. Mass Transfer Analysis: Model Derivation

To arrive at a quantitative assessment of mixing between the gas and liquid phases in the microreactor, mass transfer coefficients can be calculated and compared with values reported in the literature. In order to have an accurate comparison of performance, the same methodology used in the literature for determining the mass transfer coefficient was employed. The accuracy of a particular model in describing the mass transfer is not as important as consistency between the study here and the results available in the literature. Provided the method of analysis is the same, mass transfer coefficients measured in the microreactor can be used to make a direct comparison of performance with conventional reactors.

The result of using a heterogeneously catalyzed multiphase reaction is that several mass transfer resistances are possible. Figure 5-1 depicts schematically the different mass transfer steps for a gas-liquid-solid reaction.

Figure 5-1. Mass transfer resistances for gas-liquid-solid reaction. The hydrogen must transport to the gas-liquid interface, dissolve within the liquid, transport to the bulk liquid (gas-liquid mass transfer), transfer from the bulk liquid to the surface of the catalyst particle (liquid-solid mass transfer), and diffuse within the pores of the catalyst to the active metal sites (represented by the effectiveness factor $\eta$).
For multiphase reactions, the overall reaction rate can be expressed in terms of a sum of these resistances in series. The mass transfer resistances for gas-transport consist of diffusion within the gas-phase to the gas-liquid interface, gas absorption into the liquid, diffusion of the dissolved gas from the bulk liquid to the catalyst surface, and diffusion of the species inside the porous catalyst. Each of these will be treated individually, although gas-liquid absorption is consistently treated as the most significant resistance. The treatment follows that of Fogler.\[59\] Diffusion of the liquid reactant can also present a resistance if its concentration is low (such as at high conversions or dissolved substantially within a solvent). For the treatment here, the concentration is high enough that diffusion of the liquid will not be significant. This also allows the analysis to concentrate on transport of the gas reactant, where most of the resistance will occur during absorption into the liquid phase.

In general, a mass transfer coefficient relates the molal mass flux to a concentration gradient,

\[ N = k_i \cdot (C_i - C_b) \]  \hspace{1cm} (5-2)

Where \( N \) (mols m\(^{-2}\) s\(^{-1}\)) is the mass flux, \( C_i \) (mols m\(^{-3}\)) is the concentration of a particular species at the interface, \( C_b \) is the concentration in the bulk and \( k_i \) (m s\(^{-1}\)) is the mass transfer coefficient.\[86\] This form can be used to represent mass transport across an interface as well as within a phase, such as from the bulk to the surface of the catalyst.
5.4.1. Mass Transfer Analysis: Gas-Liquid Absorption

For the case of gas-liquid absorption, (hydrogen absorbing into a liquid stream) and using equation 5-2, \( C_i \) would be the concentration at the gas-liquid interface and \( C_b \) would be the concentration of hydrogen dissolved in the bulk of the liquid.

The total rate of gas absorption in the microreactor, \( \text{Rate}_{ab} \), depends on the total interfacial area between the gas and liquid in the reactor, \( A_i \) (m\(^2\)). The rate of absorption is the product of the flux and the area,

\[
\text{Rate}_{\text{Absorption}} = N \cdot A_i = k_i \cdot A_i \cdot (C_i - C_b) \quad (5-3)
\]

where \( \text{Rate}_{ab} \) (mols s\(^{-1}\)) is the rate of gas absorption.

Since the exact interfacial area is difficult to measure, many of the reported correlations lump \( k_L \) and \( a \) together, where \( a \) is the specific area. To get the above rate of absorption in terms of a specific area, \( a \) (m\(^{-1}\)), we would need to divide by the microreactor volume(m\(^3\)).

\[
a = \frac{A_i}{V_{\text{Microreactor}}} \quad (5-4)
\]

Substituting 5-4 into 5-3 gives:

\[
\frac{\text{Rate}_{\text{Absorption}}}{V_{\text{Microreactor}}} = k_i \cdot a \cdot (C_i - C_b) \quad (5-5)
\]

At steady state, the rate of gas absorption is equal to the rate of reaction.

\[
\text{Rate}_{\text{Absorption}} = \text{Rate}_{\text{Reaction}} \quad (5-6)
\]

For the case of cyclohexene hydrogenation, the reaction is zero order in cyclohexene and 1st order in hydrogen. Because of the assumption of steady state, and the molal flow rate...
of hydrogen greatly exceeds that required for complete conversion, the concentration of hydrogen is constant. Therefore, the rate is constant throughout the reactor and the global rate of conversion for the microreactor, from a kinetics standpoint, depends only on the amount of catalyst in the reactor. The rate of reaction can be directly measured by analyzing the rate at which the product leaves the reactor,

$$ \text{Rate}_{\text{Reaction}} = F_{\text{out}} = F \cdot X $$

(5-7)

where $F$ (mol s$^{-1}$) is the molar flow rate of substrate into the reactor, and $X$ is the conversion, 0-100%.

Substituting (5-4) and (5-5) allows one to go from the experimentally determined value for $\text{Rate}_{\text{Reaction}}$ to the rate of absorption for the gas (assuming there are no other diffusional resistances).

$$ \frac{\text{Rate}_{\text{Reaction}}}{V_{\text{Microreactor}}} = k_1 \cdot a \cdot (C_i - C_b) $$

(5-8)

What remains is the unknown value for the bulk concentration in the liquid, $C_b$. Ultimately, it can be related to the concentration on the surface of the catalyst, and hence the intrinsic reaction rate, through the liquid-phase mass transfer.

The entire volume of the microreactor is used in this analysis to arrive at a 'volumetric' reaction rate. In most cases, the volume of the liquid phase in the reactor is used. If the concentration of the substrate before and after reaction is used to arrive at a reaction rate, then the residence time within the reactor is required. For a given flow rate, the entire
empty volume of reactor provides a conservative estimate. In actuality, portions of the volume are filled with catalyst (porous) as well as gas.

Alternatively, we could divide the above expression by the density of catalyst in the volume of the reactor, \( \rho_v \), to get the rate of reaction per mass of catalyst. This reactor mass density is equal to the product of the density of the catalyst, \( \rho_c \), and the fraction of the reactor volume that is solids.

\[
\rho_v = \frac{\text{Mass}_{\text{Catalyst}}}{V_{\text{Microreactor}}} = \frac{3 \text{ mg}}{4 \mu \text{L}}
\]

\[\rho_v = (1 - \varepsilon_v) \cdot \rho_c \quad (5-10)\]

where \( \varepsilon_v \) is the void fraction and \( \rho_c \) is the density of the catalyst particles.

The result is,

\[
\frac{\text{Rate}_{\text{Reaction}}}{V_{\text{Microreactor}}} \cdot \frac{V_{\text{Microreactor}}}{\text{Mass}_{\text{Catalyst}}} = \frac{1}{\rho_c \cdot (1 - \varepsilon_v)} \cdot k_1 \cdot a \cdot (C_i - C_b)
\]

\[\frac{-r_A}{\rho_c \cdot (1 - \varepsilon_v)} = \frac{1}{\rho_c \cdot (1 - \varepsilon_v)} \cdot k_1 \cdot a \cdot (C_i - C_b) \quad (5-12)\]

where \(-r_A\) is the reaction rate per mass of catalyst, mol s\(^{-1}\) g cat\(^{-1}\).

Equation 11 is the form that can be found in Fogler's analysis for trickle-bed reactors (equation CD12-2). This form is not required for the analysis since the mass of catalyst would cancel out, leaving only the volume of the bed, as in equation 7.

In all treatments of multiphase mass transfer, the gas and liquid phases are assumed to be in equilibrium directly at the interface. Consequently, \( C_i \) can be represented by the saturated solubility of the gas in the liquid phase, a property easily
measured. This saturated solubility of the gas is related to the pressure in the gas phase at
the interface by Henry's law:

\[ P_s = H \cdot CH_2 \] \hspace{1cm} (5-13)

In some cases, the concentration of the gas-phase reactant at the gas-side of the interface
is itself limited by transport within the gas-phase. The rate of gas-side mass transfer can
be represented by,

\[ \text{Rate} = k_e A (P_b - P_i) \] \hspace{1cm} (5-14)

For the sake of completeness, the gas-side mass transfer is included, but is negligible for
this analysis. The gas-phase is pure hydrogen and the flow of hydrogen is in considerable
excess relative to the stoichiometric amounts required by the reaction..

5.4.2. Mass Transfer analysis: Liquid Film resistance

Lumping the liquid film resistance into the overall mass transfer coefficient
provides a conservative estimate for the gas-liquid absorption mass transfer. To see what
contribution, if any, the liquid diffusion might have, several calculations were performed.
The first is to use the classical Frossling correlation, which relates the Sherwood number
to the Reynolds number for flow past a sphere. This correlation is typically used in the context of a slurry reactor, where the catalyst particles can be treated as independent spheres within the fluid media. The applicability to packed-beds of the Frossling correlation is debatable, but is presented here for reference. Other, more complicated correlations exist in the literature, but determining the applicability of those correlations is beyond the scope of this thesis. The second approach, which represents the absolute minimum, is to assume a solid surface area equivalent to that of the microstructured reactor, and then to estimate the mass transfer coefficient on the basis of stagnant diffusion.

The Frossling correlation provides one estimate for $k_c$:

$$Sh = \frac{k_c d_p}{D} = 2 + 0.6 \times Re^{1/2} \times Sc^{1/3}$$  \hspace{1cm} (5-15)

For a liquid flow velocity of 0.1 cm/s (corresponding to a flow rate of 0.1 mL/min the 10 channel device) the Reynolds number is 0.05. (based on a characteristic length of 50µm)

The Schmidt number for hydrogen in organics is approximately 50.
Table 5-1. Values of the Sherwood number for various Reynolds numbers

<table>
<thead>
<tr>
<th>Re</th>
<th>Sc</th>
<th>Sh</th>
<th>$k_c$(cm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>50</td>
<td>2.5</td>
<td>0.08</td>
</tr>
<tr>
<td>1</td>
<td>50</td>
<td>4.2</td>
<td>0.14</td>
</tr>
<tr>
<td>10</td>
<td>50</td>
<td>9.0</td>
<td>0.28</td>
</tr>
</tbody>
</table>

($D = 50\,\mu\text{m}, D = 1.6 \times 10^{-4}\,\text{cm}^2/\text{s}$)

Calculation of $a_p$

The surface area per volume reactor of the catalyst particles can be estimated by assuming a spherical shape for the particles and assuming a void fraction in the reaction channel, $\varepsilon$ of 0.4. In this case,

$$a_p = \frac{4\pi R^2}{4 \times \frac{4}{3} \pi R^3} \times (1 - \varepsilon) = \frac{3}{R} (1 - \varepsilon)$$

<table>
<thead>
<tr>
<th>R</th>
<th>$\varepsilon$</th>
<th>$a_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25,\mu\text{m}</td>
<td>0.4</td>
<td>720 cm$^2$/cm$^3$</td>
</tr>
</tbody>
</table>

For $Re = 0.05$, $k_c a_p = 58\,s^{-1}$

The packed bed is in fact a loosely ordered arrangement of near-spherical particles with a distribution of particle sizes. Mass transfer to a submerged sphere may give an approximate measure, but cannot take into account the flow effects of adjacent particles and voids. The finite volume of gas within the voids also makes an accurate
measure of the diffusion length (approximated by the particle diameter in the Sherwood number) difficult. Particles completely enveloped by gas will have a shorter boundary layer than particle clusters which receive little gas flow.

Calculation of the surface area may actually be a very good estimate. In order for the diffusing species to reach the catalyst sites within the pores of the catalyst, they will have had to diffuse through that surface area defined by the diameter of the particle.

**Lower Bound Analysis for Liquid Diffusion**

The liquid-solid mass transfer coefficient, $k_c$, relates the flux of a species from the bulk liquid to the surface of the catalyst:

$$N = k_c \cdot (C_b - C_s)$$  \hspace{1cm} (5-16)

or

$$\text{Rate(liquid transfer)} = k_c \cdot a_c \cdot (C_b - C_s)$$  \hspace{1cm} (5-17)

Assuming that diffusion takes place through a mass transfer layer surrounding the catalyst particle, then according to Fick's law:

$$N = \frac{D_{AB}}{\delta} \cdot (C_b - C_s)$$  \hspace{1cm} (5-18)

Where $D_{AB}$ is the diffusivity of species A in the liquid and $\delta$ is the layer thickness. For thin film theory, the mass transfer coefficient can be estimated from the diffusivity if the length scale for diffusion is known. Because the solid particles are known to be well dispersed throughout the reactor volume, the diffusion path from a liquid segment to any solid surface will be short relative to the dimensions of the channel. This diffusion path
from the bulk liquid to any solid surface will not be larger than the size of any voids in the solid packing. As such, the diameter of the particle is the appropriate length scale, similar to the case for the Frossling correlation. For the diffusivity of hydrogen in organics, \( D_{AB} = 1.6 \times 10^{-4} \text{ cm}^2/\text{s} \), and a diffusion length, \( \delta = 50 \mu\text{m} \), then \( k_c = 0.032 \text{ cm/s} \). The minimum value for the solid surface area per volume of reactor can be determined as above, considering a void fraction of 0.5, which gives \( a_p = 600 \text{ cm}^{-1} \) and:

\[
k_c a_p \text{ (minimum)} = 19.2 \text{ s}^{-1}
\]

5.4.3. Mass Transfer: Internal Pore Diffusion and Effectiveness Factor

The established method for assessing diffusion within the porous catalyst is to use an effectiveness factor, \( \eta \), which is a function of the Thiele modulus, \( \phi \). The rate for this first order reaction is then expressed as,

\[
R = \eta k C_{H_2}
\]

(5-19)

The effectiveness factor ranges from 0 to 1 and is formally defined as the ratio of the average reaction rate with the reaction rate at surface conditions. For a spherical catalyst particle and first order reaction, the Thiele modulus takes the form,

\[
\phi = \frac{D_r}{2} \sqrt{\frac{k S_a \rho_p}{D_e}}
\]

(5-20)

where \( k \) (cm/s) is the first order surface reaction rate constant, \( S_a \) (cm\(^2\)/g) is the active surface area per mass of catalyst, \( \rho_p \) (g/cm\(^3\)) is the catalyst density, and \( D_e \) is the effective
diffusivity in the porous catalyst. The square of the Thiele modulus represents the ratio of the characteristic time for diffusion to the characteristic time for the reaction. Kawakami and co-workers determined the effective diffusivity of hydrogen and cyclohexene in porous alumina catalysts, $D_e = 2.7 \times 10^{-5}$ cm$^2$/s. [79] Using this diffusivity and the reaction rate constant determined by Madon, $k_{sur} = 2.8 \times 10^{-3}$ cm/s, the Thiele modulus was calculated. For a 50 µm diameter spherical catalyst particle, $\phi = 1.9$. The relationship between the Thiele modulus and the effectiveness factor for a spherical catalyst and a first order reaction is,

$$\eta = \frac{3}{\phi^2} (\phi \coth \phi - 1)$$  \hspace{1cm} (5-21)

Using equation 5-21, the effectiveness factor is 82%. The effectiveness factor for a typical catalyst pellet with a diameter of 1mm is 8%. Consequently, for this fast reaction, internal diffusion is likely to be rate limiting using standard catalyst pellets. An additional benefit to using the microreactor, in addition to improved gas-liquid absorption, is the reduced diffusional limitations within the pores of the catalyst as a result of using small 50 µm diameter particles.

5.4.4. Mass Transfer Analysis: Steady State Rate Expression

At steady state, the concentration of hydrogen in the liquid phase, as well as hydrogen adsorbed to the catalyst is assumed to be constant. The rate of gas absorption into the liquid as well as the rate of diffusion balances the rate of reaction at the surface of the catalyst. Equating equations 5-3, 5-14, 5-17, and 5-19 and eliminating the bulk
liquid concentration provides a rate expression in terms of the mass transfer coefficients, the intrinsic rate constant and the saturated solubility of hydrogen.

\[-r_A = \frac{1}{\left( \frac{1}{H \cdot k_s \cdot a} + \frac{1}{k_1 \cdot a} + \frac{1}{k_c a_p} + \frac{1}{\eta k} \right)} \cdot C_A^{\text{SAT}} \quad (5-22)\]

\(C_A^{\text{SAT}}\), the equilibrium solubility of hydrogen, related to the pressure by Henry's constant \(H\), Henry's constant

\(k_s\), gas-side gas-liquid mass transfer coefficient

\(k_1\), liquid-side gas-liquid mass transfer coefficient

\(k_c\), liquid-solid mass transfer coefficient

For all of the analysis here, the gas phase consists of pure hydrogen. Consequently, gas-side mass transfer can be considered negligible and can be eliminated from the rate expression.

For simplicity of analysis, we could also lump the mass transfer resistances into a single diffusional resistance which is limiting the reaction rate,

\[\frac{1}{K_L a} = \frac{1}{k_1 \cdot a} + \frac{1}{k_c a_p} \quad (5-23)\]

Therefore, the rate expression reduces to:
\[-r_A' = \frac{1}{\left( \frac{1}{K_L \cdot a} + \frac{1}{\eta k} \right)} \cdot C_A^{\text{SAT}} \quad (5-24)\]

In the analysis of mass transfer, the reaction rate, \(-r_A\), is determined experimentally. \(C_A^{\text{SAT}}\) is a property available in the literature, \(k\) is the intrinsic rate constant estimated previously. From the rate data then, estimates for \(K_L a\) can be made. Distinguishing between \(K_L\) and \(a\) is difficult to do experimentally. Classical gas-liquid reactor analysis uses homogeneous gas-liquid reactions to determine the interfacial area, \(a\). The homogeneous gas-liquid reaction is difficult to adopt here, as discussed in section 5-3. Some form of a quench is required in order to stop the reaction once it has left the reactor. Integrating a quench reaction onto the chip complicates the reactor design and operation and therefore operating a homogeneous gas-liquid reaction is beyond the capabilities of the present devices.
5.5. **Mass Transfer Coefficients in the Microreactor**

Using equation 5-24, the rate data from tables 4-2 and 4-3, and accounting for solubility changes with the pressure, the following mass transfer coefficients can be determined. If the rate taken from the work of Madon et al. can be considered the intrinsic rate, then the mass transfer coefficients can also be calculated for the batch reactions. The intrinsic rate for the 5% Pt/Al₂O₃ catalyst was determined in this manner. The intrinsic rate for the 1% Pt catalyst, as determined from the literature value in Madon et al., was used to determine the $K_{i,a}$ of the batch experiments. Assuming that the $K_{i,a}$ is the same for all batch experiments (the vessel, stirring speed, catalyst concentration and particle size were all the same) then the intrinsic rate for the 5% catalyst can be determined as in Table 5-2. The overall mass transfer coefficient was found to be in the range of 3-15 s⁻¹ for the 1% Pt/Al₂O₃ catalyst. In determining the specific contribution to mass transfer by gas-liquid absorption, the gas-liquid absorption mass transfer coefficient, $k_{i,a}$, could be as high as 33 s⁻¹ if the minimum rate for liquid-solid mass transfer is assumed. Overall these values for the mass transfer coefficients compare very favorably to values reported in the literature for other laboratory scale reactors.
Table 5-2. Mass Transfer coefficients calculated in the microreactor

<table>
<thead>
<tr>
<th></th>
<th>Reaction Rate at 1 atm</th>
<th>M (g/cm³)</th>
<th>Intrinsic Rate Constant (m)</th>
<th>kₐₐₐₐ</th>
<th>kₐₐₐ</th>
<th>kₐₐₐ</th>
<th>kₐₐₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1% wt Pt/ Al₂O₃, Multichannel Reactor, Maximum Observed Rate</td>
<td>2.00×10⁻⁶</td>
<td>0.83</td>
<td>13.28</td>
<td>1</td>
<td>∞</td>
<td>10.3</td>
<td>10.3</td>
</tr>
<tr>
<td></td>
<td>2.00×10⁻⁶</td>
<td>0.83</td>
<td>13.28</td>
<td>0.82</td>
<td>∞</td>
<td>12.4</td>
<td>12.4</td>
</tr>
<tr>
<td></td>
<td>2.00×10⁻⁶</td>
<td>0.83</td>
<td>13.28</td>
<td>0.82</td>
<td>2</td>
<td>32.7</td>
<td>32.7</td>
</tr>
<tr>
<td>1% wt Pt/ Al₂O₃, Multichannel Reactor, Minimum Observed Rate</td>
<td>9.10×10⁻⁷</td>
<td>0.83</td>
<td>13.28</td>
<td>0.82</td>
<td>∞</td>
<td>3.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Batch Reaction w/ 1% Pt/ Al₂O₃</td>
<td>1.43×10⁻⁶</td>
<td>0.0054</td>
<td>0.0864</td>
<td>0.82</td>
<td>∞</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Batch Reaction w/ 5% Pt/ Al₂O₃</td>
<td>2.60×10⁻⁶</td>
<td>0.0036</td>
<td>0.11</td>
<td>0.82</td>
<td>∞</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Maximum Observed Rate 5% wt Pt/Al₂O₃</td>
<td>1.4×10⁻⁶</td>
<td>1.075</td>
<td>32.90</td>
<td>0.82</td>
<td>∞</td>
<td>8.1</td>
<td>8.1</td>
</tr>
<tr>
<td>Minimum Observed Rate 5% wt Pt/ Al₂O₃</td>
<td>2.80×10⁻⁷</td>
<td>0.825</td>
<td>25.25</td>
<td>0.82</td>
<td>∞</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

 collaborated on the basis of kLₐ

5.6. Rate of Gas Absorption versus Mass Transfer Coefficients

Mass transfer coefficients have been used throughout reactor design as a means for accurately scaling up processes and predicting reaction performance for a given process configuration. In comparing two reactors, however, mass transfer coefficients
alone may not give an accurate view of performance. For heterogeneously catalyzed gas-
liquid reactions, the loading density of the catalyst (mass of catalyst per reaction volume)
defines the reactor type and whether or not mass transfer coefficients can be directly
compared. For example, the packed-bed microreactors in this study can be accurately
compared with trickle-bed reactors, were the catalyst loading for both reactor designs is
near 0.5-1 g/cm³. A slurry reactor, on the other hand, has a much lower catalyst loading
(0.001 g/cm³) and consequently a much lower volumetric rate. The lower volumetric
rate means that the requirements for gas absorption are reduced and the slurry reactor
may not be mass transfer limited, even though the $K_{La}$ is orders of magnitude lower.

The following example should make this more clear. Consider the same reaction,
the same catalyst, and the same amount of catalyst, 40 mg. The reaction is run in 40 mL
of substrate in a slurry reactor versus in a microreactor of 40 µL volume. For a $K_{La}$ of 1
s⁻¹ in either reactor, the maximum rate of hydrogen mass transfer is $3.6 \times 10^{-6} \text{ mol/cm}^3/\text{s}$. (where the solubility of hydrogen is $3.6 \times 10^{-6} \text{ mol/cm}^3$)

\[
\text{Rate(max)} = k_{La}(C_{H_2}^{\text{sat}}) \quad (5-25)
\]

The intrinsic reaction rate (at $C_{H_2}^{\text{sat}} = 3.6 \times 10^{-6} \text{ mol/cm}^3$) is $5.7 \times 10^{-5} \text{ mol/s/g cat.}$

\[
\text{Rate(intrinsic)} = (k_{su}S_A)C_{H_2} \quad (5-26)
\]

In the slurry reactor, where the catalyst loading would be $1 \times 10^{-3} \text{ g/cc}$, the reaction rate is
$5.7 \times 10^{-8} \text{ mol/cc/s}$ (almost 2 orders of magnitude less than the maximum hydrogen mass
transfer rate). In the microreactor, where the catalyst loading is 1 g/cc, the reaction rate is 5.7×10^{-5} \text{ mol/cc/s} which is now higher than the maximum rate of hydrogen mass transfer. In order for the reaction to proceed at the rates observed in this study (1.4×10^{-5} - 2.3×10^{-5} \text{ mol/cc/s}), the $K_La$ value must be larger than 1 \text{ s}^{-1} in the microreactor.

The important criteria in determining the mass transfer limitations is the rate of gas absorption in the reaction volume relative to the rate of reaction per volume. At first glance, it may seem appropriate to simply compare the rate constants (in this case $KLa(s^{-1})$ and $\eta k (-16s^{-1})$). For the case of the slurry reactor where $KLa = 0.001$ \text{ s}^{-1}, it would appear that mass transfer limitations predominate even though its actually not the case. The volumetric rate constant $k$, is defined in terms of the catalyst loading density which varies between the reactors. To assess this relative influence, we define a parameter $\Psi$, which is a ratio of the maximum rate of gas absorption in the reaction volume to the maximum intrinsic volumetric reaction rate:

$$\psi = \frac{K_La \cdot C_{H_2}^{Sat}}{\eta k \cdot \mu (C_{liq})^x (C_{H_2}^{Sat})^y A_{cat} m}$$  \hspace{1cm} (5-21)

Where $m$ is the catalyst loading density, $x$ is the order of the reaction for the liquid reagent and $y$ is the order of the reaction for the gaseous reactant. Table 5-3 compares $\Psi$ for various reactor configurations and mass transfer coefficients.
Table 5-3. Comparison of mass transfer coefficients for various reactors.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>$K_a$</th>
<th>$m$</th>
<th>$k_{surf} (x=0, y=1)$</th>
<th>$A_{cat}$</th>
<th>$C_{H_2}^{sat}$</th>
<th>$\Psi$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>s$^{-1}$</td>
<td>g/cm$^3$</td>
<td>cm/s</td>
<td>cm$^2$/g</td>
<td>mol/cm$^3$</td>
<td></td>
</tr>
<tr>
<td>Packed-bed Microreactor</td>
<td>15</td>
<td>0.9</td>
<td>2.80×10$^{-3}$</td>
<td>5700</td>
<td>3.60×10$^6$</td>
<td>1.0</td>
</tr>
<tr>
<td>Trickle-Bed Reactor</td>
<td>0.1</td>
<td>0.9</td>
<td>2.80×10$^{-3}$</td>
<td>5700</td>
<td>3.60×10$^6$</td>
<td>0.01</td>
</tr>
<tr>
<td>Slurry Reactor</td>
<td>0.01</td>
<td>0.001</td>
<td>2.80×10$^{-3}$</td>
<td>5700</td>
<td>3.60×10$^6$</td>
<td>0.63</td>
</tr>
</tbody>
</table>

For the microreactors, the rate of gas absorption is on the same scale as the rate of reaction, which is appropriate for conducting a mass transfer analysis. If intrinsic kinetics analysis were desired, then $\Psi$ should be much larger than 1 so that gas absorption is not limiting. In making a comparison between reactors or in determining the extent of mass transfer limitation, this ratio provides a more accurate assessment relative to just comparing the mass transfer coefficients by themselves.

An important observation is that as the activity of the catalyst is reduced (the metal surface area or $A_{cat}$) $\Psi$ increases, and the importance of gas-liquid mass transfer diminishes. This suggests that to operate a reactor efficiently, the volumetric reaction rate should be reduced so as to not be limited by the gas absorption rate. To achieve overall productivity from the reactor, the total reactor volume can be made sufficiently large that the total amount of catalytic surface area meets the demands of the process. This explains the need to construct increasingly larger reactors. If space is not a premium, then the most efficient method of reactor operation is to have small specific catalyst activities and large reactor volumes.
5.7. Summary

Using traditional thin film theory to describe the mass transfer resistances in a gas-liquid-solid reaction, the mass transfer coefficients were determined experimentally for several microfabricated devices. The hydrogenation of cyclohexene to cyclohexane using a platinum supported on alumina catalyst was used as a model reaction. Using the rate data from chapter 4, the volumetric mass transfer coefficient, \( K_{La} \), was determined to fall in the range:

\[
K_{La} = 3-10 \text{ s}^{-1}
\]

Accounting for diffusion within the pores of the catalyst and assuming that mass transfer within the liquid film could be a contributing factor, the mass transfer coefficient for gas-liquid absorption was found to be as high as:

\[
k_{La} \text{ (maximum observed value) } = 33 \text{ s}^{-1}
\]

These values for the mass transfer coefficient are at least 100 times larger than values reported in the literature. But as discussed in section 5-6, mass transfer coefficients are useful only when comparing reactors with comparable catalyst loading densities, such as among packed-bed reactors. But even comparing the packed-bed microreactors of this study with conventional multiphase packed bed reactors, the mass transfer capabilities are greatly improved.
6. Microstructured Catalytic Reactors

6.1. Introduction

Micromachining technology promises the ability to create novel fluidic structures unattainable using conventional fabrication methods. The ability to create arrays of interconnected features scaling down as small as microns is the hallmark of silicon and semiconductor manufacturing methods. Although the principle use of silicon has been for electronics, silicon has been considered as a structural material for the creation of miniature mechanical devices for some time. The excellent thermal and mechanical properties of silicon, coupled with the fabrication infrastructure for integrated circuit manufacturing, makes silicon micromachining one of the leading candidates for creating the world in miniature. It provides the machinist access to a range of microscopic sizes and dimensions and can create arrays spanning orders of magnitude in size relative to the small features. So while conventional milling or laser drilling may be able to construct a single feature 0.05 mm in size, silicon micromachining can make thousands of 0.05 mm features in the space of a square centimeter—all at one time.

The packed-bed multichannel reactors in this thesis provide a good example of some of the capabilities of micromachining technology, such as the small filter unit, the parallel array of channels, the integrated thin film heaters and temperature sensors, and the fluidic manifold. But the functional unit of the reactor is still the catalyst particle which has been filtered from standard catalyst powders. The reactors are in essence, scaled-down versions of their macro-scale counterparts. The issues associated with packing and loading of the catalytic powders are the same as those faced with
conventional packed-bed reactors. The difference with the microfluidic packed-beds is that the reactor geometry can be tailored in such a way that the pressure drop for using extremely small particles is manageable. But despite the control over pressure drop, providing an even loading density among all ten channels is problematic. Slight variations lead to uneven distributions in flow and poor reactor efficiency. A reactor could be designed such that the pressure drop is determined from the microfluidic channels, rather than the packed bed of particles. Since the microfluidics are precisely defined, the flow distribution is guaranteed to be evenly distributed provided the pressure drop of the packing is much smaller than the pressure drop of the microfluidics. This approach, however, limits the overall size of the reactor and compromises reactor productivity. As seen in chapter 4, even for reaction channels 2 cm in length, the pressure drop can be near 10 psi. In order to provide distributed flow, the channels either have to be made much shorter, or the pressure drop required would exceed the capabilities of the experimental setup (section 2.5). Another approach to achieving evenly distributed flow is to integrate the catalytic support structures directly into the walls of the reaction channel. The reactor design presented in this chapter is an illustration of a chemical reactor which would not have been possible without micromachining methods.

For fast multiphase reactions, the rate and selectivity of the chemical process can be greatly influenced by the mass transfer limitations of one reagent's transport within and across phases. Using silicon micromachining technology, reactor devices have been constructed that demonstrate improved mass-transfer for gas-liquid heterogeneously
catalyzed processes.[87] In these devices, standard catalyst particles 50-75 µm diameter were loaded into silicon channels with an integrated filter unit. While the small particles provide the high surface areas for improved gas-liquid mixing, they also represent a challenge in terms of pressure drop and fluid distribution among the ten parallel channels. Expanding upon that work, the next generation of reactors presented here, consist of integrated catalyst supports, as opposed to packed-beds. The channels are patterned with arrays of columns, 50 µm in diameter, 300 µm tall, with nearly 20,000 columns per device. Figure 1-1 shows one of these parallel channel devices and figure 6-1 shows the microstructural features within the channels. By constructing these microstructured channels, a packed bed is simulated where the geometric properties (support size, shape and distribution) are controlled. As a result of the extreme uniformity of the packing arrangement, control over fluid flow is greatly enhanced. Since fabrication of the columns is straightforward using deep reactive ion etch technology, the challenge then becomes incorporating the catalyst into these structures such that the activity is comparable to that of the standard catalysts. The microstructured channels also provide for enhanced visual characterization of two-phase flow in microchannels.

The ability to construct arrays of microstructural features using silicon microfabrication has been investigated for other applications. It has been found that surfaces composed of arrays of micro columns exhibit dramatic differences in wetting characteristics.[88] In that study, only columns with diameters smaller than 32 µm exhibited ‘ultra hydrophobicity,’ that is a contact angle considerably higher than smooth silicon, relative to smooth surfaces or even arrays of larger columns. The primary difference with that study and the work here is that the water-air flow is on top of the
surface, as opposed to through the columns of the microreactors here. But it is important to point out that as a result of engineering the microtextures of the surfaces that dramatic differences in gas-liquid behavior can be achieved.

Both packed-beds and microstructured channels have appeared before in the context of microfluidic systems and will likely continue to find application in microfluidic analysis and reaction.[89, 90] In one case, the surface of the columns was used to abstract and collect DNA from flowing solutions.[91] In another case, the surface of the microfabricated channels was functionalized to perform the chromatographic separation.[92] For heterogeneous catalytic applications, the activity is greatly enhanced if the catalytic component is supported upon a porous layer. Creating this highly active layer within microreaction devices has received attention from several groups.[93-95] Janicke and co-workers[94] used a CVD method to obtain porous alumina layers in their microreactors Laurell and co-workers[95] have demonstrated porous silicon as a support structure for their immobilized enzyme reactors. The activity of the enzyme reaction is greatly enhanced over the non-porous channels as a result of the increase in surface area. In a device presented here, the microstructured silicon channels have been made porous in a similar fashion and impregnated with a platinum catalyst for the multiphase hydrogenation reactions. Whereas features of the present work have appeared in other contexts, the fabrication and application are unique, particularly in the case of the multiphase mass transfer analysis.
6.2. Microstructured Reactor Device Design

In order to construct a chemical system on a chip, the following features were desired:
a) the ability to mix multiple reagents, whether of the same phase or different phases b) the ability to heat the reaction zone and measure the temperature and c) the ability to incorporate catalytic activity whether by standard catalytic particles or integrated catalytic layers. Two similar devices have been designed toward this end. Both consist of multiple reaction channels connected in parallel. In the first design, the channels (300 μm deep, 625 μm wide, 20 mm long) are empty and contain a filter structure near the exit to retain a packed-bed of catalytic particles (Figure 6-1A). The second device contains staggered arrays of 50 μm columns within the channels to provide both catalyst support and static mixing (Figure 6-1B).

Figure 6-1. CAD illustration of the two reactor design options.
A) Open channel with filter for filling with catalytic particles.
B) Microstructured channel with staggered arrays of columns
6.2.1. **Multiphase Microfluidics Design**

The first function for the reaction devices described in the present work is to mix two reagents on-chip. As discussed in chapter 2, a number of strategies have emerged for passively mixing fluids at these scales owing to the laminar nature of the fluid flow.[48-52] The goal is to reduce diffusional lengths and generally this is done by splitting up and interleaving the inlet streams. Another strategy, with an added level of fabrication complexity, makes use of chaotic advection[53, 54] The approach taken here uses the continuous flow split and mix strategy.

Mixing multiple phases, such as a gas and liquid, at the microscale is more problematic: interfacial forces cause the phases to rapidly coalesce. Keeping the fluids dispersed in order to reduce diffusional length scales is considerably more difficult as compared to mixing two liquids of similar physical properties. Nevertheless, improved gas-liquid contacting has been demonstrated in this and other microchannel applications.[41, 70] As the dimensions of the device shrink, capillary forces have more of an impact on fluid flow. The Young-Laplace equation, \( \Delta P = 2\gamma/r \), can be used to estimate the minimum pressure needed to overcome surface tension(\( \gamma \)) effects for a gas-liquid interface in a small channel.[71] For a 10 \( \mu \)m channel radius and water (\( \gamma = 72 \) dyn/cm), \( \Delta P = 0.14 \) atm. Therefore, the dimension for the inlet mixing channels (25 \( \mu \)m wide) is not so small that surface tensions effects would become prohibitive.

The 10 reaction channels are 2 cm long, 600 \( \mu \)m wide, and 300 \( \mu \)m deep. Each of the ten channels is connected by a 500 \( \mu \)m wide channel running perpendicular near the inlet. The multitude of inlet streams first meet here and this region is considered the ‘mixing zone.’ The channel has been retained for the microstructured reactor, although

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its function for delivering the catalyst slurry is no longer required. In fact, the presence of this open channel prior to the reaction channels may be deleterious. After separating the two phases into 90 separate, interleaved inlet streams, the gas and liquid flows rapidly coalesce before meeting at the reaction channel.

At the end of the 2 cm long channels are filter structures consisting of 40 \( \mu \text{m} \) wide columns with a separation gap of 25 \( \mu \text{m} \). After the filter, the fluids exit via a 400 \( \mu \text{m} \) diameter port to the bottom silicon layer, where all ten exit streams are collected to a single port. The difference between the packed-bed device and the microstructure one is simply the arrays of columns patterned into the channels; all the other fluidics are the same.
6.2.2. Microstructured Catalyst Design

For the microstructured device, the ten reaction channels contain the integrated catalyst support structures as seen in Figure 6-1. Figure 6-2 is a scanning electron micrograph of the actual reaction channels containing these columns. The posts, 50 μm in diameter and 300 μm tall, are arranged in staggered arrays and provide for a void fraction of 60%. Compared with packed-beds, which for spherical packing have a void fraction of 40%, the microstructured channels will have a reduction in pressure drop with only a small reduction in catalyst volume. The geometry of the posts (cross-section and spacing) was chosen for simplicity and ease of fabrication. A denser arrangement of posts could be possible, depending on the limits of the DRIE process. These micromachined features, in conjunction with the gas-liquid inlet distributors, serve to provide a high surface area for improved gas-liquid contacting.

In order to attain comparable catalytic activity with the standard catalytic particles, it is necessary to increase the surface area even further. This could be accomplished by coating with a porous layer, or, as in the devices here, create a porous layer within the substrate itself. Methods for making silicon porous are readily integrated into a fabrication process.

The microstructured design is unique to microfabrication; such a design with small, high aspect ratio features, would be impractical, even for a prototype, to manufacture using conventional machining methods.
Figure 6-2. SEM of DRIE etched microstructured reaction channels. The scalloped surface of the post is due to etch process which consists of alternating chemistries.
6.3. Fabrication

The fabrication for the microstructured reactor is similar to the multichannel device with the exception of a few steps required for integrating porous silicon. All the masks are the same except for the one which defines the microstructured reaction channels. As a result, some of the design features have been inherited from the multichannel reactor, such as the catalyst inlet ports, the catalyst loading channels, and the filter structure at the end of the channels. Although the filter structure no longer serves any functional role, the geometries between the multichannel and the microstructured reactors are identical in order to make a direct comparison in reaction performance. The microstructured reactor involves the use of a silicon nitride layer as mask for the electrochemical etching process which forms the porous silicon.[96] Figure 6-3 depicts the process flow outlining the six major fabrication steps. Silicon nitride, 5000 Å thick, was deposited onto the silicon wafers using a vertical tube furnace (VTR). Onto the silicon nitride was spin coated the thick resist to 10 µm (Figure 6-3, step 1). An SF₆ plasma process (Applied Materials Precision 5000) was used to etch the silicon nitride (Figure 6-3, step #2). The deep channels were then formed in the silicon on both sides using the same STS etch process as before (Figure 6-3, step #3). A thin layer of aluminum (2000 Å) was added to the back of the wafer to provide uniform electrical contact during the porous silicon formation process (Figure 6-3, step #4). After creating the porous silicon (step #5), the aluminum was removed from the backside using a PAN etch (10:3:1 phosphoric acid, acetic acid, nitric acid) for about 1 hour. The wafer was rinsed with methanol and deionized water before returning to the clean room where it was cleaned using 3:1 H₂SO₄:H₂O₂ at 90°C. Oxidation of the porous silicon was performed at
two different conditions following procedures reported elsewhere. [97, 98] Using a furnace tube, the wafer was subjected to an oxygen atmosphere at 300 °C for 3 hours. The second oxidation condition involved the 300 °C, 3 hour oxidation followed by 1 hour in oxygen at 850 °C.

**Figure 6-3.** Process flow for the fabrication of microstructured channels incorporating porous silicon.

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Pattern 10um thick resist on 5000Å SiN</td>
</tr>
<tr>
<td>2.</td>
<td>Pattern SiN</td>
</tr>
<tr>
<td>3.</td>
<td>Pattern silicon (both sides)</td>
</tr>
<tr>
<td>4.</td>
<td>Deposit aluminum to backside</td>
</tr>
<tr>
<td>5.</td>
<td>Create porous silicon</td>
</tr>
<tr>
<td>6.</td>
<td>Remove aluminum and anodic bond glass to topside</td>
</tr>
</tbody>
</table>

SiN □  Photoresist □  Porous Si □  Al □  Glass □
A glass wafer was then anodically bonded to the silicon wafer at the same conditions as before without removing the silicon nitride layer (step#6). Although performance of the bond to silicon nitride relative to bare silicon was not characterized, bond success and uniformity was unaltered. Others report on the versatility of the anodic bond in relation to oxide or nitride layers on the silicon.[99]

6.4. Porous Silicon as a Catalyst Support

6.4.1. Introduction

The goal of the microstructured reactors was to simulate the packing of a fixed-bed reactor while precisely defining the packing geometry so as to improve fluid distribution, heat and mass transfer. To incorporate the heterogeneous catalyst, either the columns have to be coated with an active material, or consist of active material within their volume. The approach taken here was to make the columns porous and impregnate them with the catalyst. Alternatively, a process could be envisioned where the columns are directly fabricated out of a porous material. Arrays of features made of thin-film porous silica have been demonstrated, but the height was only 0.2 µm.[100] The columns here are 300 µm tall, and currently there are no methods available for fabricating them in a porous material. Another alternative would be to coat the columns with a porous material such as a sol-gel alumina coating common with wash-coats of monolithic reactors.

Numerous studies on porous silicon and its formation mechanisms have been performed, with primary interest focused on its photoluminescent properties. Recent work has also focused on sensing applications: the ability to integrate silicon
microelectronics with a high surface area sensor makes porous silicon an attractive material. [101, 102] Surface areas have been reported as high as 800 m$^2$/g, which is comparable to standard catalyst supports.[103] Almost all of the applications in microdevices for porous silicon has been for sensing applications. The enzyme microreactors of Drott et al. are the first example of using porous silicon as a catalyst support.[95, 104-107] To date, porous silicon has not been investigated as a catalyst support for noble metal catalysts. Only one study has modified porous silicon with palladium, but the application was for hydrogen detection.[108]

Porous silicon is formed through an electrochemical etching process. The rate of formation, the pore size and morphology, and porosity of the layer depend upon a number of parameters, including the etch solution, the dopant type and density of the substrate, the current density, and the presence of illumination. A number of reviews describe in detail the chemistry and influence of these parameters on the porous silicon formation process.[109, 110] Figure 6-4, taken from a paper by V. Lehman, illustrates the dependence of the average pore size on both dopant type and density.[111] N-type wafers were chosen for the devices here in order to achieve "meso-porous" material where internal diffusion would not be limiting. The evolution of hydrogen gas is characteristic of pore formation, while the absence of gas evolution is characteristic of electropolishing.[109] For all of the devices etched here, significant gas evolution was noted.
Figure 6-4. Resulting pore size in porous silicon for different dopant types and wafer resistivities, taken from [111].

To create the porous silicon in the channels only, silicon nitride was used as a mask to protect the surface of the wafer. This ensured a smooth surface for the subsequent anodic bond. The silicon nitride was kept on the surface after the etch because it was feared that the long phosphoric acid etch, commonly used to strip silicon nitride, would damage the porous silicon. The procedures used for making the porous silicon are similar to those reported elsewhere.[103] The patterned silicon wafers, n-type, with varying resistivity of 10-20 $\Omega$-cm or 1-5 $\Omega$-cm, received an aluminum coating on the backside for contact, which was removed after the porous silicon was formed. Illumination was used and a current density of roughly 15 mA/cm$^2$, based on the open
area of silicon, was applied for 10-30 minutes. Scanning electron micrographs were used to characterize the depth of the etch into the substrate.

Oxidation of the porous silicon was also accomplished by means of a tube furnace prior to anodic bonding. Others report that a treatment at 300 °C in oxygen stabilizes the porous silicon.[98] [112] Subsequent higher temperature oxidations convert more of the porous layer to oxide while sacrificing some of the porosity of the layer. Without this oxidation step, a native oxide layer (1.5 nm - 4 nm thick) will spontaneously grow upon the freshly etched porous silicon with exposure to air.[113] Yet another approach to oxidizing the porous silicon is an anodization process.[114] In addition to its stabilizing effect upon the porous layer, converting more of the silicon to silicon oxide makes the catalytic support better resemble traditional high-surface area silica supports.

6.4.2. Experimental Procedure for Porous Silicon Formation

The essential requirements for forming the porous silicon are making an electrical contact to the backside of the wafer and keeping the acid solution with electrode on the front-side. Figure 6-5 depicts the arrangement of the fixture for holding the wafer and the experimental set-up. The fixture was specially designed for this application and was based off a similar design for performing KOH etching of silicon wafers. Figure 6-6 shows the teflon fixture and the arrangement of a Hypalon™ o-ring for making the seal to the silicon wafer. The wafer is compressed against this teflon fixture by another teflon piece and o-ring with the aid of several Kel-F hex screws. Once sealed, the acid solution (100 mL consisting of 50:50 by volume, ethanol and hydrofluoric acid) is poured into the
fixture and the top electrode immersed. A standard halogen lamp light source with fiber optic guide was used for illumination.

![Diagram](image)

**Figure 6-5.** Experimental set-up for creating porous silicon. The wafer is compressed between two o-rings housed within a teflon vessel. Contact is made to the backside aluminum layer and a platinum electrode is immersed in the electrolyte solution.

The difficulty in using wafers after channels have been etched on both sides, is that the through holes do not allow the retention of the acid on the front-side. For this reason a 'handle-wafer' was used. The handle-wafer was a 100 mm diameter silicon wafer with a 2 cm diameter hole etched through the middle. When attached to the device wafer with a thin layer of photoresist (then baked at 90C for 30 minutes) the handle wafer covered the through-holes while allowing contact to the backside of the wafer. Electrodes were fixed to the backside aluminum film with the aid of conducting carbon-tape. The platinum electrode immersed in the acid solution consisted of a platinum gauze (3 cm diameter, parallel to the wafer) attached to a platinum wire.
The procedures for incorporating the platinum catalyst within the porous silicon follow standard methods of catalyst preparation.[115, 116] Impregnation of the platinum catalyst was performed on an individual die by flowing the precursor solution (1-10wt% H₂PtCl₆ in DI water) through the reactor. The devices were allowed to dry for several hours at 70°C before calcination. After the water had been removed, the reactors were heated in air at 550°C for 3 hours, and then the catalyst was reduced by flowing pure hydrogen at 300°C for another 3 hours.

Figure 6-6. Teflon reactor for creating porous silicon on 4" wafers. 16 hex-nut screws compress the oring against the silicon wafer.
6.5. Device Characterization and Results

6.6. Catalyst Characterization and Chemisorption

Figure 6-7 shows an optical micrograph of a cross section of a reactor after creating the porous silicon. The same cross section is shown using a scanning electron micrograph in Figure 6-8. The pore structure penetrates approximately 50 μm into the silicon substrate. Although the surface of the columns appeared to be roughened, it was difficult to determine their porosity, if any. There is slight undercutting of the silicon nitride mask, evidenced by the taper near the interface. To evaluate various catalyst preparation conditions, in addition to the reaction rate, the surface area of the platinum metal in the device was determined using a pulsed carbon monoxide chemisorption method.[117, 118] Carbon monoxide selectively chemisorbs onto the platinum only, and based on the volume of CO adsorbed, the surface area can be determined. Using this technique, standard 1%Pt/Al₂O₃ catalyst particles loaded into the open channel device produced a measured surface area of 300cm². Under the same conditions, surface area for the platinum on porous silicon was measured as 100cm², while no detectable adsorption was observed for empty reactors or porous silicon reactors without the platinum.
Figure 6-7. Photomicrograph of the cross-section of the reaction channels indicating the depth of the porous silicon layer into the bulk silicon substrate.
**Figure 6-8.** SEMs of porous silicon. A) Shows inset for enlarged view in B) Macropores are visible in the walls of the channel. C) Magnified view of the macropores indicating a size approaching 0.5mm. D) Shows inset for magnified view in E) Micropore formation at the base of the channel.
6.6.1. Surface Area Characterization

Commercial supported metal catalysts are characterized by a number of parameters including pore size distribution of the support, total surface area of the support, metal particle size and dispersion and surface area of the active metal.[117] Measurements are made using standardized equipment. Metal surface area is important in predicting the activity of a catalyst since it provides the total number of surface sites available for reaction. It is useful in making comparisons of catalysts, since it can provide an estimate of the activity in the absence of mass transfer limitations. Chemisorption methods are routine since gases like CO and hydrogen bond specifically to certain metals and not to the porous support.

Static volumetric methods are the most common and are explained here briefly. A known weight of catalyst is introduced to a glass sample tube of known volume. After the sample is evacuated, a certain volume of the adsorbate gas is introduced. When adsorption equilibrium is attained, the amount of gas remaining in the system can be determined from the pressure measurement. Keeping the temperature constant, the volume of adsorbed gas is measured for increasing pressures.

The principal limitation for this approach is the amount of catalyst required to make an accurate measurement. Depending on the volume of the glass sample tube, increasingly accurate pressure measurements are required for small sample weights, or low surface areas. This limitation becomes prohibitive for the microreactors of this study, because a single microreactor has a relatively small amount of total surface area. For example, a ten-channel reactor can hold approximately 40 mg of catalyst, while typical measurements using the volumetric approach call for catalyst weights of 1000 mg.
6.6.2. Pulsed Chemisorption Methods

Another established method for determining surface areas is a pulsed chromatographic chemisorption approach[119, 120] A continuous flow of inert gas passes through the catalyst in a packed bed arrangement. Pulses of CO are continuously injected into the flow stream. In the absence of any adsorbing metals, the pulses eluted will contain the same volume of adsorbing gas, as all of the adsorbing gas flows to the detector. In the presence of an adsorbing metal such as platinum or palladium, a fraction of the volume of the initial pulses will be irreversibly adsorbed to the catalyst and the volume of the pulses eluted will be reduced. As the pulses are continuously injected, the catalyst becomes saturated with the adsorbing gas and the volume of the adsorbing gas gradually returns to its injected value. Figure 6-9 is an example of a chromatogram illustrating the pulsed chemisorption approach. The difference in volume from an eluted pulse and the volume of a pulse at saturation is the amount of CO adsorbed. By summing up over all the pulses, the total amount of CO adsorbed, and hence the surface area of the catalytic metal can be determined. What makes this approach particularly suitable for the microreactors is that the volume and content of the injected pulses can be tailored according to the amount of metal area exposed. In this case, the amount of CO per pulse was set to be approximately equal to the amount that would be required to completely cover the surface of the catalyst. The other advantage is that the sensitivity of the detector, in this case a mass spectrometer, allows for a relatively small amount of CO per pulse.
Figure 6-9. CO Chemisorption pulse chromatogram. Each pulse of CO is injected into the flow through the reactor, eluted, and measured on the mass spectrometer. The initially clean platinum surface irreversibly adsorbs CO from the first several pulses. Eventually the surface is saturated and the pulses approach a steady volume eluted.

Figure 6-10 illustrates the experimental setup for the pulsed chemisorption analyses. A Hewlett Packard gas chromatograph (HP GC6980) with mass selective detector and gas sampling valve was adapted for this application. A gas sampling valve with an injection volume of 1mL was used to inject 5000 ppm carbon monoxide in helium into a carrier gas of helium. A control valve was used to maintain a steady pressure of 1 or 5 psig of CO in the sample of loop of the injection valve. A manifold containing the packaged microreactor and a bypass line was inserted into the oven of the
GC and connected to the inlet port upstream and a 30 meter capillary column downstream. The column was used to create a pressure drop between the turbo pump of the mass spec (1.4×10⁻⁵ torr) and the microreactor. As a result, the pressure in the microreactor was constant at 11.2 psig for a flow of 1.5 sccm. The pressure drop across the microreactor was negligible for this flow rate of gas. Pulses were injected every 2.5 minutes and the average retention time was 1.4 minutes.

Figure 6-10. Experimental set-up for CO chemisorption analysis. A 1 mL sampling valve injects the CO pulses into the flow stream where the flow can either bypass the reactor or travel through the reactor and adsorb to the catalyst. The capillary column is used to create a pressure drop from the exit of the reactor to the vacuum conditions within the mass spectrometer.
Figure 6-11 contains the results for several samples, including an empty microreactor, a porous silicon microreactor with no catalyst, a porous silicon reactor with platinum catalyst, and a multichannel reactor loaded with 1% Pt/Al₂O₃ catalyst. The results are tabulated for each pulse as a fraction of the steady state volume. The volume adsorbed for each pulse is equal to the difference between the pulse volume and the volume of the pulses at saturated, steady-state conditions. Given a pressure in the sample loop of 5 psig, a sample volume of 1 mL, and a temperature of 30 C, the ideal gas law provides for 2.2×10⁻⁷ mols of CO per pulse of 5000 ppm CO in helium. The surface area can then be determined, assuming that each CO molecule is chemisorbed to one platinum atom and each platinum atom provides approximately 1.2×10⁻¹⁵ cm² of surface area.[117].

The measured surface areas (relative error of approximately 20%) for the various devices were 240+/− 48 m² for the 1 wt% Pt/Al₂O₃ powder, 103 +/- 20 m² for the porous silicon impregnated with platinum, and 0 m² for the empty porous silicon reactors. On a per mass basis, the surface area for the powdered catalyst was 1.1 m²/g which is considerably lower than the value measured using a conventional static volumetric approach of 5.7 m²/g. The important consideration though, is that the pulsed CO chemisorption provides an accurate comparison between the number of available catalytic sites between the two different types of reactors.
Figure 6-11. Results for CO chemisorption experiments. The commercial porous catalyst adsorbs the most CO followed by the porous silicon reactor. The control experiments consisting of an empty reactor and a porous silicon reactor with no platinum adsorb almost no CO.
6.7. Gas-Liquid Reaction Results in the Microstructured Reactor

The catalytic hydrogenation of cyclohexene to cyclohexane was chosen as a model reaction for a number of reasons. The reaction is fast at room temperature and atmospheric pressure, so it is likely to have some degree of mass transfer limitation. The reaction has been used extensively for characterizing industrial multiphase reactors, and many of the fluid properties are known. Hydrogenations are ubiquitous throughout fine chemicals and pharmaceutical processing, and because hydrogen is only slightly soluble in most organic solvents, mass transfer of the hydrogen to the liquid phase can often be the rate-limiting step. Hydrogenations are exothermic and the explosive potential of pressurized hydrogen makes the safety aspects of a miniaturized reaction unit attractive.

Results for the reaction rate and mass transfer coefficient in the microstructured reactor are compared here with the packed-bed device. In chapters 4 and 5, it was shown that mass transfer could be greatly improved in packed-bed microreactors where catalyst particles were 50 μm in diameter. In typical laboratory reactors, such three-phase reactions can be limited by the rate of gas absorption into the liquid, the distribution of reagents throughout the packed-bed, or by diffusion within the porous catalyst itself. An overall mass transfer coefficient, $K_{L\alpha}$, was measured in the microfabricated packed-bed to be near 10 s$^{-1}$, more than 100 times larger than values reported for laboratory scale reactors. For these packed-bed devices, achieving an even distribution and packing density among the parallel channels was critical in order to get an even flow of reagents. Otherwise, the flow may bypass one or several channels, decreasing the utilization of the reactor. Furthermore, the packing density is affected by the particular mode of catalyst
loading. Obtaining a repeatable packing density among several devices operated in parallel could become problematic. In order to alleviate some of these challenges typically associated with packed-beds, the microstructured reactors of this chapter mimic the packed-bed while providing exact control over the bed properties. The high degree of tolerance offered by microfabrication methods ensures that each reactor has the same flow behavior.

The reaction rate results for several devices are presented in Figure 6-12. All of the microstructured devices exhibit significant decay of catalytic activity over the initial start-up of the reaction process. For comparison, the results using a conventional 5 wt% Pt catalyst are shown to be significantly better than the porous silicon catalysts. After an initial decay, the reaction rate decreased slightly for the case of the reactor 2C in Figure 6-12. After subjecting the device to air at 300 °C for 1 hour followed by another reduction, the activity remained slightly lower than the previous level of activity, indicating that the oxidation did not 'reactivate' the catalyst.
Figure 6-12. Cyclohexene hydrogenation in the porous silicon reactors.

This non-oxidized porous silicon reactor was then used at a temperature of 50 °C. Once the reaction rate decayed significantly, the device was purged with hydrogen for two hours at 50 °C and a portion of the activity was regained. This behavior was repeated three times, as seen in Figure 6-13 which plots the time course for the catalyst activity. The result is that purging the reactor with hydrogen eventually regained some of the lost catalytic activity. In addition, a porous silicon reactor was tested which was subjected to an oxidation treatment at 800 °C for 1 hour. The reaction results indicate that the activity is more stable, but the reaction rate is reduced. This is most likely due to a reduction in catalytic surface area when the small pores of the porous silicon are closed due to oxide growth.

Initial reaction rates for the hydrogenation of cyclohexene in an integrated catalytic microreactor (non-oxidized porous silicon) were observed to be $2.0 \times 10^5$
mol/min., nearly a third that of the 10 channel packed-bed reactor. When normalized for the metal content of the device, the reaction rate compares favorably: $6.5 \times 10^{-4}$ mol/min/m$^2$ with the porous silicon support versus $4.5 \times 10^{-4}$ mol/min/m$^2$ with the powdered catalyst. Figure 6-14 compares the catalytic activity for the various devices. The conclusion is that mass transfer in the microstructured reactor is equivalent to that of the packed-bed, even though the pressure drop is less. Furthermore, the overall activity of the microstructured reactor is much lower than the conventional catalysts because of the amount of active metal impregnated into the porous silicon. The calculated mass transfer coefficients, $K_{La}$, in the integrated microstructured reactor fall within the range of 3-7 s$^{-1}$.

**Figure 6-13.** Lifetime studies for porous silicon with platinum catalysts. Oxidized porous silicon is more stable, but has a lower activity than the non-oxidized porous silicon.
Figure 6-14. Comparison of reaction rates and normalized activities between the packed bed reactors and the porous silicon reactors. Top) Global reaction rates. Bottom) Reaction rates normalized for catalytic surface area.
6.8. Summary

The design, fabrication, and characterization of multiphase microfluidic devices has been presented. Using silicon microfabrication methods, a "fully micromachined" packed-bed reactor has been constructed. Columns, 50 μm in diameter, have been etched into the channels of the microreactor, mimicking the arrangement of a packed bed. Procedures for creating porous silicon have been used to provide a high surface area support for the metal catalyst. Such microfabrication methods allow the integration of catalyst supports or gas-liquid contacting structures directly into the reactor. This provides an added level of control on such factors as support size and distribution and void fraction, as compared to a typical packed-bed reactor. The microfluidic construction of the reactor allows for the controlled distribution of gas and liquid reagents to either the small catalyst particles or the microstructured posts. In addition, silicon microfabrication has allowed the local integration of temperature sensing and heat generation in the reactor device. And while the packaging has a critical impact on the performance of the heaters, it has been demonstrated that on-chip temperature control is feasible with improved packaging methods.
7. Gas-Liquid Contacting in Microfabricated Systems

7.1. Introduction

Microfabrication methods provide a means for constructing novel channel geometries for the purposes of influencing gas-liquid flow. The nature of the flow, in terms of the various flow regimes, relative hold-up of the two phases, and pressure drop have been extensively studied at the macroscale (tubes, packed tubes) as well as at the meso scale (glass capillaries). As the size of the channel decreases, the effects of gravity diminish and the role of surface tension takes over. The ability to construct channels with microstructural elements, such as the microstructured reactor of this thesis, provides for the first time, the ability to influence and control two-phase flow in microchannels for the purposes of increasing interfacial areas and reducing pressure drop.

The issue of flow regimes in packed-bed multiphase reactors was addressed briefly in Chapter 2. The design of the microstructured reactor, with a void fraction significantly larger than that of a packed bed, puts the reactor somewhere in between an open channel and a densely packed-bed in terms of characterization. Before the specific flow behavior is addressed, gas-liquid flow in macro-scale systems is presented to provide a background for the results that follow.

7.2. Gas Liquid Flow Behavior in Conventional Systems

The phenomenon of gas-liquid two-phase flow occurs in a variety of situations, including absorption for the purification of a gas stream, reaction for the conversion of a liquid reactant, and heat exchange with phase change, such as in the rod bundle of a nuclear reactor. The parameters that are critical for the process are the two-phase
pressure drop and the rate of mass or heat transfer. Both of these parameters are
dependant upon the physical nature of the flow. The nature of the fluid flow, as
determined by the physical form that the fluids conform to, the relative volume of the two
phases and the interfacial contact area, ultimately affects the efficiency of thermal and
mass transport between the phases. Before any attempt at predicting pressure drop or
transport efficiency can be made, the specific flow regime must be known. Some
examples of flow behavior in channels with gas and liquid flowing co-currently are
illustrated in Figure 7-1.

Flow regimes are characterized by mapping the physical form of the flow onto a
domain containing the superficial velocity of the gas versus that of the liquid. The types
of flow regimes as well as the transitions between them depend upon the physical
properties of the fluids involved as well as the size and shape of the channel. For two-
phase flow in tubes the flow behavior can range from ‘Bubble’ flow, where the gas is
dispersed as discrete bubbles within the liquid to ‘Annular flow,’ where the liquid flows
along the channel walls and the gas flows in the center. Intermediate to these two, is a
‘slug-flow’ or ‘Taylor-flow’ regime where the phases form discrete slugs separated by
regions of the alternate phase. If the channel is large enough, then gravitational forces
influence the flow and the fluids will form ‘Stratified’ layers based on their relative
densities. For high gas and liquid flow rates, Xu et al. report a “churning / turbulent”
flow in which the gas is chaotically dispersed and the flow trajectories vary in time.[121]
Figure 7-1. Two-phase flow regimes in tubes and capillaries, taken from [25, 121]. At small relative gas velocities, bubbles exist within a continuous liquid phase. Increasing the gas flow rate leads to slug or Taylor flow then to annular flow. At sufficiently high velocities, 'churn' flow or dispersed flow exists. For large tube diameters, gravity serves to 'stratify' the two phases.

One of the earliest works on two-phase flow in capillary tubes was performed at MIT by Mikio Suo and Peter Griffith. [122] In that work, the flow transition between slug flow and annular flow were described and a theoretical model for predicting the transition provided. Since then, much work has been performed and the complex nature
of the flow is still the subject of investigation. [121, 123, 124] The work by G.I. Taylor has made 'Taylor' flow synonymous with the slug-flow fluid regime. [125]
7.3. Hydrodynamics and Flow Regimes of Two-Phase Microchannel Flow

The nature of the two-phase gas-liquid flow was investigated for a range of flow rates and materials. Understanding the flow behavior is critical in determining the extent of mass transport and characterizing the microstructured microreactor relative to its macroscale counterparts. The nature of the flow, as well as the transition from various flow regimes, depends not only on the relative velocities of the two phases, but also on the various physical properties of the solvent (viscosity, surface tension). The behavior of the gas-liquid interface, as determined by hydrodynamics of the two-phase flow, will affect the interfacial area for gas-liquid contacting and consequently the rate of mass transport between the two phases. Water-air mixtures were investigated in order to compare results with those studies found in the literature. A variety of organic solvents and air were also used since they more closely represent the hydrogenation reactions intended for the microstructured device. Gas-liquid flow behavior was also investigated for the open-channel device, since the results were more likely to parallel the results of the prior work in two-phase microchannel flow.

7.3.1. Microstructured Reactor Flow Regimes

Figures 7-2 through 7-4 contain a series of photomicrographs that illustrate the various flow regimes that have been observed in silicon (un-oxidized) microstructured channel reactors. Although some of the terminology to describe these flow regimes has been adopted from other studies of gas-liquid flow, the exact nature of the flow may not be entirely identical. The presence of the columns within the channels forces the flow to behave with slight differences in some cases, as will be noted in the following discussion.
The flow regime which predominates at relatively small gas and liquid flow rates is the *slug-flow regime*. At relatively low gas flow rates, the predominate phase is liquid and the gas travels as slugs, or bubbles, of various sizes among the ten channels (Figure 7-2).

![Slug-flow regime](image)

**Figure 7-2.** Slug-flow regime in a microstructured reactor using co-current flow of ethanol / air. Flow distribution is even to all ten channels. Inset shows a single slug of gas with a flat frontal profile.

As the gas flow rate is increased relative to the liquid flow, streams of gas form in the center of the channels, as the liquid prefers to wet the walls of the channels, termed here as the *annular-flow regime*. In cylindrical capillaries, annular flow describes the concentric arrangement of the two phases, with the liquid phase wetting the walls of the capillary. As seen in Figure 7-3, the rectangular geometry of the channels forces the liquid to the either end of the 600-μm-wide channel. It has been observed that the middle
portions of the channel contain the gas-phase only, so the wetting of the channel walls is uneven and skewed toward the corners of the channels.

Figure 7-3. Annular flow in a microstructured reactor using ethanol and air. The liquid phase is confined to the walls of the reactor and the gas follows a path (sometimes tortuous) through the center of the channels. All ten inlets are distributing gas and liquid phases.

Increasing both flow rates produces a flow regime that is characterized by a rapid dispersion of both phases (Figure 7-4). It is in this flow regime that mixing of the gas and liquid phases is the greatest and the interfacial area is expected to be substantially larger than in an open channel arrangement.

Figure 7-5 plots a flow regime map for water-nitrogen contacting in an unoxidized silicon microstructured reactor. The flow regime and pressure drop were recorded at various combinations of the flow rates for the gas and liquid streams. From this collection of data points, the map was constructed illustrating the transition between
the various flow regimes. A number of observations can be made. First, the dispersed flow regime, which occurs at both high gas and liquid flow rates, borders both the slug flow and the annular flow regimes. The transition from slug flow to dispersed flow is not as distinct as with the ethanol mixtures: channels contain both flow types as the flow transitions to complete dispersion in all ten channels. Figure 7-6 illustrates the slug-dispersed flow regime. Unlike with the ethanol-air mixtures, at both low liquid and gas flow rates the water-air flow is a mixture of annular and slug flow. The flow gradually transitions to the annular flow as the gas flow rate is increased for a given liquid flow rate.

**Figure 7-4.** Dispersed flow regime. The defined gas-liquid interface of the annular flow regime is broken with a high degree of dispersion of the gas and liquid phases. Whereas the gas-liquid interface was fixed with the annular flow, here it randomly fluctuates throughout the volume.
Later in this chapter the interfacial contact areas are analyzed and the dispersed flow regime is found to have almost an order of magnitude increase in the interfacial area. The flow rates required to generate this dispersion, however, are quite high. A water flow rate of 2-3 mL/min. is required, corresponding to a very small residence time in the reactor (~1 second).

Figure 7-5. Flow regime map for water-nitrogen mixing in a silicon microstructured reactor. Data points represent observed flow regimes. Transition lines are estimated based upon the closest data points.

Dispersed Flow■, Annular Flow♦, Slug-dispersed ■, Slug-Annular □
Figure 7-6. Slug-dispersed flow regime in a silicon microstructured reactor. Several channels exhibit dispersion, while the others exhibit slug flow. Due to a distribution of velocities among the ten parallel channels, transitions between flow regimes do not occur simultaneously among all the channels.

7.3.2. Influence of wetability of the surfaces on flow regimes

The gas-liquid flow behavior was characterized in reactors with different surface compositions to determine the influence of the wetability of the reactor surface on flow transitions. It has been found in the generation of oil in water emulsions in microchannel devices that the hydrophobicity of the channels can influence the level and uniformity of dispersion.[126] To determine the influence of the wetability of the channels on gas-liquid flow behavior, oxidized silicon and anodized silicon (porous silicon) reactors were used and flow maps generated. In a previous study, it was found that anodized silicon could be made extremely hydrophobic as a result of the surface roughness.[127] The
water-air-surface contact angle was measured as high as 100 degrees for anodized silicon, 60 degrees for silicon, and near zero for oxidized silicon. A completely hydrogen terminated silicon surface is hydrophobic (θ = 90) but after exposure to air and growth of a native oxide, it becomes slightly hydrophilic (θ = 60)[127]. As a result, the oxidized microreactors are likely to be more hydrophilic than normal silicon, while the porous silicon reactors are likely to be more hydrophobic.

Figure 7-7 is a flow map for an oxidized (5000 Å thermal oxide) silicon reactor. Slight variations from the un-oxidized silicon reactor was observed in terms of the nature of the flow regimes as well as the transitions. The most notable effect was the reduction in the liquid flow rate for the transition point to dispersed flow. The estimated transition point is 0.5mL/min in the oxidized (more hydrophilic) versus 2.5 mL/min in the un-oxidized channels. This can be rationalized by the energy required to disperse or break the gas-liquid interface. For a hydrophilic surface, a lower energy (lower velocity) is required to force the water to wet more of the surface. The other notable effect was in the size and shape of the slugs. For the hydrophilic surface, the slugs tended to be larger and more elongated as opposed to the more hydrophobic silicon surface for which the gas phase formed smaller, more frequent slugs. The results for the porous silicon channels did not have a notable difference on the flow behavior or transition points. The flow closely resembled that of the bare silicon surface.
Figure 7-7. Flow regime map in an oxidized microstructured reactor. The more hydrophilic surface and its influence on flow regimes can be compared with that of the non-oxidized silicon in Figure 7-6.

In conclusion, the parameter most effected by the surface and fluid properties is the mean slug size in the slug and slug-dispersed flow regimes. The transition from one flow regime to another was only slightly affected with the most pronounced affect between the oxidized and non-oxidized silicon reactors.
7.3.3. Open Channel Gas-Liquid Flow

The two-phase flow behavior in the open, ten-channel device described in chapter 3 contrasts with that of the microstructured devices of this chapter. The relative flow rates or the ratio of gas to liquid flow was critical in determining an even distribution of flow among the ten parallel channels. Channeling, or poor flow distribution, was prevalent whenever one of the flow rates was greatly in excess relative to the other. Figure 7-8 maps out the regimes where evenly distributed flow occurred.

![Two-Phase Flow Patterns, Open Channel (Water/Air)](image)

**Figure 7-8.** Flow regime map in an open-channel microreactor using water/air co-current flow. For relatively low flow rates of either phase, channeling and poor distribution occurs.
For gas flow rates of 20 sccm (v = 1 cm/s) and lower, several channels were deficient in the gas phase. Gas would distribute in the forms of slugs to some, but not all of the channels. Only as the flow rate is increased above a certain threshold (independent of liquid flow rate) would the two phases equally distribute among the ten channels. At sufficiently high liquid and gas flow rates, two-phase flow would be evenly distributed. The flow in that case would resemble the ‘annular flow regime’ with liquid flowing predominately at the sides of the channels. Figure 7.9 is a photomicrograph of the annular flow in the open-channel reactor. The liquid deficient flow regime was characterized by an excess of gas flow such that the liquid would trickle or form rivulets of flow around the channel walls. The liquid flow was pulsatile in nature and did not distribute evenly among the ten channels.

![Figure 7.9. Photomicrograph of ‘Annular’ flow in an open-channel microreactor.](image-url)
The implications for this flow behavior for gas-liquid reactions is that the presence of the columns facilitates the even distribution of the two phases. In addition, an entirely new flow regime, that of the dispersed flow in Figure 7-4, is created as a result of the posts. This dispersed flow regime was not observed in the open-channel reactors for the range of flow rates studied.

7.3.4. Pressure Drop Measurements

In addition to observing the specific flow regime, the pressure drop was measured for a range of gas and liquid flow rates. The two-phase pressure drop for various solvents with air is plotted in Figure 7-10 as a function of liquid flow rate. For a constant gas flow rate of 100 sccm, the flow transitions to the dispersed flow regime near 2mL/min. As the flow makes the transition, the pressure drop takes a sudden shift upwards. Upon decreasing the flow rate, the pressure drop continues along this upper curve until the flow transitions back to the annular flow. The hysteresis effect in the pressure drop profiles is a result of the unstable nature of the transition between various flow regimes. The pressure drop for a range of flow gas and liquid flow rates is plotted in Figure 7-11 for water-air mixtures in an un-oxidized silicon reactor. This can be compared with the various flow regimes of Figure 7-5. For changes in the volumetric flow rate, the liquid has more of an influence on the pressure drop. The effect becomes more severe as the gas flow rate is increased.
Figure 7-10. Two-phase pressure drop in the microstructured reactor (gas flow rate = 100 sccm). The pressure drop is linear with liquid flow rate, but shifts when the flow transitions to the dispersed flow regime.
Figure 7-11. Two-phase pressure drop in the microstructured reactors using water/air cocurrent flow. On a volume basis, increasing the gas flow rate has a more severe impact on the pressure drop.
7.3.5. Interfacial Area Determination

Using the optical images shown in Figures 7-2, 7-3, and 7-4, the interfacial contact areas were estimated. Both the size of the bubbles as well their number density were used to estimate a contact area per volume of device. The contact area for the flow regime in Figure 7-2 is estimated at 1500 m$^2$/m$^3$ while the area for Figure 7-4 is estimated at 16,000 m$^2$/m$^3$. These numbers are considerably larger than reported values of 200 m$^2$/m$^3$ for bubble columns in chemical processing. [25]

Two-phase flow in capillaries has been shown to produce a similar range of flow regimes, from "slug flow," where the gas is in the form of discreet bodies encompassing the channel, to "annular flow," where the gas is steady stream through the center of the channel.[128] The microstructured reactor, by introducing surface forces in the center of the channel, provides an added measure of control over the two-phase flow and flow transitions. MEMS fabrication methods allow this engineering of internal capillary surfaces for the purposes of increasing heat transfer to the substrate and influencing two-phase flow to increase mass transfer across phases.

The pressure drop for the microstructured channels were measured for co-current flow of gas and liquid phases. The dispersed flow regime in Figure 7-4 occurred for a flow rate of ethanol of 2mL/minute and a nitrogen flow rate of 100 standard cm$^3$/minute. At these conditions, the pressure drop was measured as 0.54 atm. Reaction conditions, however, dictated much smaller flow rates (0.2mL/min of cyclohexene, 20sccm of H2) and consequently the pressure drop was almost negligible for the microstructured channels.
7.3.6. Discussion: Geometry influence

As a result of using photolithographic methods to define the channel and feature geometries, a number of variables in the geometry could be altered to affect the nature of the two-phase flow. For instance, the presence of the ‘mixing zone’ or open channel running perpendicular to the reaction channels where the 90 inlet channels first meet could influence the flow. The consequence of this open channel is that the two phases have the opportunity to coalesce before being constrained again within the confines of the column arrays. If the reaction channels were to begin directly at the point where the inlet channels meet, the two phases could be induced to remain segregated because the wetting of the columns would counteract the forces causing the phases to separate. Another variable is the size and spacing of the posts. As both the size and spacing is reduced, the surface area is increased and the void fraction is reduced. A higher pressure drop will be required for a given velocity and the result could be that the onset of dispersed flow occurs at a much lower velocity. This is critical for reactions, such as the cyclohexene hydrogenation, which require longer residence times for appreciable conversion. For the cyclohexene hydrogenation, the residence time required is large enough that the velocities of the phases results in flow within the non-dispersed flow regimes.
7.4. Summary

Gas-liquid two-phase flow was investigated in the microstructured reactors for a variety of flow rates, materials, and surface compositions. Flow regime maps were generated for both the open channel reactor design and the microstructured channel reactor design, and notable differences in flow behavior occurred. Even flow distribution was more difficult to achieve in the open channel design. With the microstructural elements, even flow distribution was achieved and a dispersion of the two phases was generated at flow rates above 2 mL/min. The two-phase pressure drop was determined for a range of gas and liquid flow rates and was always within a manageable value (<50 psig) for liquid flow rates up to 10 mL/min. It was demonstrated that the interfacial contact area between the gas and liquid phases was substantial: as high as 16,000 m\(^{-1}\). This, like the mass transfer coefficient product \(K_La\), was more than 100 times larger than those achieved in typical industrial gas-liquid contactors. By increasing the surface area over which the gas and liquid streams must contact, mass transfer limited reaction rates can be improved. For reactions that are limited by the mass transfer effects, as is the case with many multiphase reactions, the improvement in mass transfer offered by the microreactor translates into improved overall reaction rates, reactor performance and control.
8. Multiphase Microreactor Comparison and Discussion

8.1. Mass Transfer Coefficient Comparison

The observed reaction rates for the cyclohexene hydrogenations in this microreactor study all exceed expected rates on the basis of conventional mass transfer capabilities. Even if the reactions were completely controlled by mass transfer, such as the rate of absorption of hydrogen into the liquid, the mass transfer coefficients are still orders of magnitude larger than conventional laboratory and industrial multiphase reactors. The analyses of chapter 5 and 6 provide explicit values for the volumetric mass transfer coefficient, $K_{L}a$, using a thin-film model approach. Table 8.1 summarizes these mass transfer values in the microreactors and compares them with conventional multiphase reactors and some of the other micro device studies. Compared with these conventional multiphase reactors, the microfabricated reactors of this study have mass transfer coefficients that are at least 100 times larger.

**Table 8-1.** Comparison of multiphase reactors.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>$K_{L}a$ ($s^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microreactor: Packed-bed</td>
<td>3-30</td>
<td></td>
</tr>
<tr>
<td>Microreactor: Integrated Catalyst</td>
<td>3-10</td>
<td></td>
</tr>
<tr>
<td>Trickle bed reactor</td>
<td>0.005-0.01</td>
<td>[25]</td>
</tr>
<tr>
<td>Trickle bed (high pressure)</td>
<td>0.01-0.8</td>
<td>[30]</td>
</tr>
<tr>
<td>Bubble column reactor</td>
<td>0.005 - 0.01</td>
<td>[25]</td>
</tr>
<tr>
<td>Slurry reactor</td>
<td>0.02 - 0.2</td>
<td>[25]</td>
</tr>
<tr>
<td>Jet-loop reactor</td>
<td>0.01 - 2.2</td>
<td>[25]</td>
</tr>
<tr>
<td>Tube (4mm I.D.)</td>
<td>0.1-8</td>
<td>[124]</td>
</tr>
</tbody>
</table>
8.1.1. Why is the mass transfer coefficient, $K_{L,a}$, 100 times larger?

One of the principle motivations for microreaction technology is that shorter diffusional lengths and higher surface to volume ratios translate into improved mass transfer rates. The interfacial area, a, is itself a surface to volume ratio. It is the surface area of contact between the gas and liquid phases per volume of reactor. If the liquid wets all of the solid surface in a reactor and the gas flows through all of the interstitial space, then the interfacial contact area will scale with the surface area of the reactor. For packed-bed contacting devices, the surface area scales with that of the spherical packing, where the surface to volume ratio of a sphere is $1/6R$. In the laboratory scale reactors for which the mass transfer coefficients were reported, the particle size was near 5mm. For the particle sizes of the microreactor, 0.05 (100 X smaller) the surface to volume ratio is 100 X larger. Thus if the interfacial contact area, a, scales with the surface area of the packing, then the increase in $K_{L,a}$ could be accounted for in terms of the surface area alone.

In addition to the surface area, the mass transfer coefficient itself, $k_L$, may also contribute. If the mass transfer coefficient is approximated assuming a stagnant layer for diffusion, then $k_L \sim D/\delta$, where $d$ is the length scale for diffusion. If this length scale for diffusion again scales with the characteristic length of the packing, then the expected increase would be on the order of 100 for the 50 um and smaller particles used in this work.

To summarize, both $k_L$ and a scale inversely with a characteristic length. Assuming that the same characteristic length (diameter of the packing) determines the surface area for gas-liquid contacting as well as the length scale for diffusion then,
\[ K_L a \approx \frac{1}{L^2} \]  

(8-1)

For the reduction in particle size from 5mm to 50um, it is conceivable that the mass transfer coefficient could increase as much as a factor of 10,000.

8.2. Interfacial Gas-Liquid Contacting Area

Determining the interfacial area, \( a \), using conventional chemical methods is difficult to adapt to the microreactor owing to the fast reactions required and the necessity for integrating the detection method on-chip. However, owing to the 2-D geometry of the microstructured reactors, an estimate of the interfacial area can be made on the basis of optical micrographs taken for the various flow regimes. This does not account for the time variation of the interface nor the relative volumes of the two phases. But for purposes of order of magnitude comparison with industrial reactors, the values are instructive. Table 8-2 lists the interfacial areas observed from chapter 6 along with representative values for various reactors available in the literature.[25] The volumespecific interfacial areas generated in the microreactors are 10-100 times larger than the conventional gas-liquid contacting devices.
Table 8-2. Interfacial gas-liquid contact areas in the microstructured reactor.

<table>
<thead>
<tr>
<th>Reactor / Flow Regime</th>
<th>Interfacial Area, a, m⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microstructured Microreactor /</td>
<td>1,600</td>
</tr>
<tr>
<td>Slug flow</td>
<td></td>
</tr>
<tr>
<td>Microstructured Microreactor /</td>
<td>5,000</td>
</tr>
<tr>
<td>Annular flow</td>
<td></td>
</tr>
<tr>
<td>Microstructured Microreactor /</td>
<td>16,000</td>
</tr>
<tr>
<td>Dispersed flow</td>
<td></td>
</tr>
<tr>
<td>Bubble Column</td>
<td>20</td>
</tr>
<tr>
<td>Packed Bubble Column</td>
<td>200</td>
</tr>
<tr>
<td>Jet-Loop</td>
<td>2,000</td>
</tr>
</tbody>
</table>

8.3. Power Dissipation

The increase in interfacial areas comes at the expense of increased resistance to fluid flow. For assessing the efficiency of mixing operations, the energy dissipation factor can be used.[129, 130] This factor accounts for the level of power input per volume of reactor for a given process. For continuous multiphase flow, the energy dissipation factor, $\varepsilon_v$ is

$$\varepsilon_v = \frac{\Delta P_{gl}}{L \cdot \mu_L} \quad (8-2)$$

where the two-phase pressure drop is used, as well as the velocity of the liquid phase. For the cyclohexene hydrogenations in the range of mass transfer coefficients recorded, the energy dissipation falls in the range:

$$(\varepsilon_v)_{micro} \sim 2 - 5 \text{ kW} \cdot \text{m}^{-3}$$

This can be compared with values for trickle bed reactors whose values range:

$$(\varepsilon_v)_{standard} \sim 0.01 - 0.2 \text{ kW} \cdot \text{m}^{-3}$$
When these two sets of energy dissipation factors are compared in light of the level of mass transfer provided, the conclusion is that the microreactor is operating as efficient, if not slightly more efficient. In fact, some of the original analyses of trickle-bed reactors attempted to correlate the mass transfer with this energy dissipation factor.[28] Satterfield proposed the following the following relation between the mass transfer coefficient and the power dissipation:

\[ k_1a = 0.017\varepsilon^{1/2} \]  

(8-3)

Figure 8-1 plots this correlation along with the range of data collected in the microreactors of this thesis. As can be seen, the mass transfer coefficients are greater than or equal to that expected on the basis of this empirical correlation. The enhanced mass transfer available in the microreaction devices comes at the expense of increased power dissipation per unit volume. But the mass transfer capabilities in the microreactors are unattainable using conventional reactor designs. As a result, the microreaction devices with enhanced mass transfer provide the opportunity for engineering more productive processes for fast reactions.
Figure 8-1. Predicted $K_La$ on the basis of power dissipation. The solid line represents data in the literature for traditional packed-bed reactor designs. The packed-bed microreactors are slightly more efficient than what is expected on the basis of Satterfield's correlation.

8.4. Discussion

8.4.1. Packed-bed or Integrated Catalyst?

The reactor design of chapter 6 presents a unique alternative for carrying out heterogeneous reactions compared with traditional packed-bed approaches. The integrated catalytic reactor allows, for the first time, a reactor which is precisely defined in terms of its packing geometry and configuration. Integrating the porous catalyst support within the walls of the reactor is a common configuration of monolithic catalytic reactors, although seldom used for the purposes of chemical synthesis. Monolithic reactors contain bundles of open channels with diameters as small as a millimeter.
Because they are manufactured using an extrusion process, the channel walls are smooth.

The principal difference in the integrated catalytic reactors here, is that, in addition to
have multiple channels or bundles of channels, the channels are filled with
microstructural features to increase the catalytic area and improve mass transfer. Both
reactor designs, the packed-bed reactor and the integrated catalytic reactor, have their
relative merits and flaws.

8.4.2. What is an appropriate reaction for a microchemical system?

There can be a number of reasons motivating the use a microreactor system,
including safety, improved thermal control, improved mass transfer and ultimately higher
productivity, improved control and sensitivity for kinetics investigations. For the chip-
based, continuous flow designs presented in this thesis, there is a minimum reaction rate
that will be feasible to perform. For process intensification and microreactors in general,
the faster the reaction the better. If the reaction is too slow, then the residence time
required for adequate conversion will require a flow rate which is too low. Several
factors determine the minimum flow rate. The capabilities of modern syringe and HPLC
pumps determines the minimum liquid flow rates for stable, reproducible pressure-driven
flow. This value is in the range of 0.001-0.01 mL/min., although some highly
sophisticated pumps can achieve flow 1-2 orders of magnitude lower. Another practical
limitation is the amount of sample required for analysis. In addition, the volume of the
packaging and fluidic interconnections can be significantly larger than the reactor
requiring significant times for the low flow rates in order to purge out the volume. Based
on the experience of the reactors studied here, a flow rate of 0.01 mL/min is the minimum
flow rate which is practical for experimentation. For a reactor volume of 0.040ml (the
multichannel reactor) the maximum residence time allowed in order to achieve a desired level of conversion is 4 minutes. For a first order reaction in a PFR with a substrate at 1M concentration, this implies a minimum rate constant (99% conversion), $k > 0.02 \text{ s}^{-1}$. If the purpose of the study is to investigate kinetics where only 10% conversion is acceptable, then the minimum rate constant is $k > 0.0004 \text{ s}^{-1}$. Fogler suggests a Damkohler number ($Da = \tau k$) of 10 to achieve a conversion of approximately 90% in a CSTR. This again would suggest a minimum first order rate constant, $k > 0.04 \text{ s}^{-1}$.

Using only rate constants, however, can be misleading. The gas-liquid hydrogenation of cyclohexene has a rate constant of 16 s$^{-1}$, but because the solubility, or concentration, of hydrogen is so low (0.004 mol/L) the corresponding rate is not as high as the rate constant would suggest. The rate is zero order in substrate until the conversion gets above 90%, then the reaction order switches to first order. Assuming zero order kinetics and a substrate of 1M, for complete conversion a residence time of only 15 seconds is required. Assuming that the hydrogen concentration does not vary substantially between various reactions, a minimum zero order rate constant can be established based on the maximum residence time of 4 minutes, $k > 1.0 \text{ s}^{-1}$.

With heterogeneously catalyzed reactions, such as the cyclohexene hydrogenation, the reaction rate can be improved by increasing the number of catalyst sites. In typical reactors, this catalyst site density is kept low or just at the point where mass transfer would limit the reaction. For the microreactor systems, the a higher catalyst activity is tolerable because the mass transfer is improved. For other reactions,
more aggressive conditions can be performed in a microreactor system, so comparing rate constants alone is not entirely accurate.

To summarize, for the reactors of this study, the follow rate constants are recommended as a guide for reactions with sufficient rate

\[ k_{(\text{min})} > 0.02 \text{ s}^{-1} \text{ (First order rate constant, liquid reaction)} \]

\[ k_{(\text{min})} > 1.0 \text{ s}^{-1} \text{ (Zero order hydrogenation)} \]

These minimum rate constants can be extended if the volume of the reactor were increased so as to increase the residence time. The volumetric limits for building microreactors using silicon micromachining technology is the size of the silicon substrate (100 mm). Assuming that a single reactor were to occupy an entire wafer, then the residence time could be improved (increased) by a factor of 10-20.

8.4.3. Is Small Really Better? The question of process intensification

Is process intensification or a reduction in reactor size beneficial? Consider the two reactors of figure 8-2. Reactor 1 has a more active catalyst at 6000 cm²/g of active surface area, while reactor 2 has a less active catalyst but is 1000 times larger. In the absence of mass transfer limitations, both will have the same reactor throughput at 6.05×10⁻⁴ mol/s for the cyclohexene hydrogenation. Because reactor 1 has the more active catalyst, it has a higher volumetric reaction rate, 6.05×10⁻⁵ versus 6.05×10⁻⁸ mol/s/cm³. If we now consider mass transfer effects, both will have the same mass transfer coefficient, \( K_{\text{La}} = 0.01 \text{ s}^{-1} \), because both are loaded with the same size catalyst pellets (5 mm). The reaction throughput for reactor 1 is now greatly diminished because the volumetric rate of gas absorption can not support the rate of reaction. This would
suggest that larger reactors are in fact more efficient, and therefore more economical, when mass transfer effects are present. Process intensification is not beneficial when mass transfer effects are not improved commensurate with the reduction in reactor size.

<table>
<thead>
<tr>
<th>Reactor 1</th>
<th>Reactor 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst = 6000 cm²/g</td>
<td>Catalyst = 6 cm²/g</td>
</tr>
<tr>
<td>Catalyst weight = 10 g</td>
<td>Catalyst weight = 10,000 g</td>
</tr>
<tr>
<td>Reaction Rate = 6×10⁻³ mol/cc/s</td>
<td>Reaction Rate = 6×10⁻⁸ mol/cc/s</td>
</tr>
<tr>
<td>Global Rate = 6×10⁻⁴ mol/s</td>
<td>Global Rate = 6×10⁻⁴ mol/s</td>
</tr>
<tr>
<td>If K_La = 0.01 s⁻¹, then</td>
<td>If K_La = 0.01 s⁻¹, then</td>
</tr>
<tr>
<td>Global Rate = 3.6×10⁻⁷ mol/s</td>
<td>Global Rate = 2.3×10⁻⁴ mol/s</td>
</tr>
</tbody>
</table>

Figure 8-2. Process Intensification Example.

The key point in this analysis is that the mass transfer coefficient stays the same. This is nearly true in most scale-up situations for trickle bed reactors. In some cases, the mass transfer coefficient may actually be higher because of the higher velocities attainable in the larger reactors. Hence the motivation for extremely large reactors is not just one of higher overall production rates, but really because the larger reactor with less
active catalyst operates more efficiently. If the smaller reactor were to have a higher mass transfer coefficient, then the volumetric gas absorption rate could support the more active catalyst, and an overall smaller reactor volume would be sufficient. The results presented in this thesis indicate that the smaller particle or catalyst dimensions translate into higher mass transfer coefficients, thereby allowing more active catalysts and consequently reduced reactor volumes. Reactor size can either refer to catalyst dimensions or reactor volume. For traditional trickle-bed reactors, reducing the reactor volume by increasing the activity of the catalyst results in poorer productivity. For reactors with small characteristic lengths such as the microreactors of this study, mass transfer is improved, and the catalyst activity can be increased resulting in a smaller reactor volume. Smaller is better—only when the features determining mass transfer are also reduced in size.

The other issue is one of deactivation of the catalyst. As seen in chapter 4, when the intrinsic kinetics of the chemistry dominate the reaction rates, as opposed to mass transfer, the global rate is more sensitive to deactivation or poisoning of the catalytic sites. In the example above, if the number of active sites in reactor 1 (mass transfer limited) is reduced by one-half, the global rate is reduced by only 0.1%. If the number of active sites in reactor 2 is reduced by one-half, the global rate is reduced by nearly 40%. By having a large catalytic activity in excess of the mass transfer capabilities of the reactor (reactor #1), the effects of deactivation can be masked and the global rate will appear to remain more constant. This comes at the expense of lower volumetric reaction rates. The net result of process intensification is that the rate per volume of reactor can be expanded greatly through improving catalyst activity and mass transfer, but
deactivation of the catalyst plays a larger role throughout the lifetime of the catalyst. As seen in chapter 4, if the proper purification and activation procedures are utilized, then the activity can remain high over time. Without deactivation, the volume of the catalyst can be tailored more efficiently to the demands of the process.

8.5. Summary

The mass transfer in the microreactor is greatly improved over its macroscale counterpart, due in part to the high gas-liquid interfacial area generated by the microreactor. The two phases are forced to mix over the catalyst in a constrained volume relative to the standard pellet-size length scale in trickle-bed reactors. Compared with the dimensions of laboratory trickle bed reactor catalyst pellets (4-8mm), the 50μm catalyst particles used in the microreactor represent a 100-fold increase in the surface-to-volume ratio. A similar improvement in performance would be expected if small particles could be used in a standard laboratory reactor. However, the use of such small particles would lead to nonuniform flow distribution and very large pressure drops for typical laboratory reactor geometries. The microfabrication approach allows the control (and visualization cf. Figure 7-4) of multiphase flows in multiple channels and geometries (higher reactor diameter to length ratios) that provide for reasonable pressure drops (0.17MPa)
9. Conclusions and Recommendations for Further Study

Conducting chemistry at microscopic dimensions has allowed the study of novel fluidic phenomena and the demonstration of unprecedented levels of mass transfer in multiphase systems. Microfabrication technology permitted the construction of the chemical reaction devices in this thesis; devices with arrays of microscopic channels and features unattainable using other, more conventional, fabrication approaches. As a result of their microscopic engineering, some of the devices allowed the study of entirely novel multiphase flow behavior: the flow regime characteristics of the microstructured reactors in chapter 7 illustrate this point. In addition, the reduced length scales allowed for rapid diffusion and higher interfacial areas producing mass transfer coefficients at least 100 times larger than in conventional reactors: the hydrogenation of cyclohexene in chapter 4 provided the quantitative verification of this effect. Yet a third demonstration in this thesis was the integration of standard catalytic materials onto a chip format as well as the integration of the catalytic materials into the reactor: this could one day allow for the rapid and automated testing of catalytic materials by integrating sensing (which is commonly a semiconductor thin-film device) and reaction into one package.

9.1. Thesis Summary

In the last 5-7 years, microreaction engineering has emerged as a new discipline as a subset of 'lab-on-a-chip' or 'micro total analysis systems.' A broad array of research activities in the area of chemical process miniaturization and intensification has taken place. As a contribution to this field of microchemical systems, this thesis has demonstrated, quantitatively, the benefits in terms of mass transfer as a result of
miniaturization. It has also been demonstrated that silicon microfabrication is a useful and enabling technology for constructing such microchemical reactors. The microstructured reactor of Chapter 6 is the culmination of a series of designs, starting with the single channel packed bed reactor of Chapter 2.

Multiphase reactions are particularly suitable for microreaction technology, whether they are gas-liquid, immiscible liquids, homogeneous or heterogeneously catalyzed. As a result of having to mix distinct phases of different fluid properties, the rates of chemical processes can often be limited or hindered as a result of the phase interface. Increasing the interfacial area between the two phases increases the rate of transport for a species and reducing the length scale by which this transport takes place also improves the rate of mass transfer. This effect is particularly evident for gas-liquid reactions which are prevalent throughout petrochemical, fine and specialty chemical and pharmaceutical processing.

Trickle-bed reactors are an example of a continuous, heterogeneously catalyzed, gas-liquid process. In addition to transport at the gas-liquid interface, mass transport effects are complicated by the fact that both reacting species must get to a catalyst site before reaction can occur. Of all the chemical reactor types, trickle-bed reactors are the most likely to suffer from mass transfer limitations. For this reason, the trickle-bed reactor was chosen as an illustrative guide and point of comparison for designing chip-based multiphase reactors. The critical issues in the design of the microreactor were the nature of the catalyst, the speed and exothermicity of the model reaction, the distribution and mixing of gas-liquid streams in confined spaces, the pressure losses, and the required residence times.
9.2. Principal Accomplishments of the Thesis

9.2.1. Measurement of $K_{L,a}$ in a microreactor system

The performance of a microreactor system was quantitatively characterized and compared with conventional reactors using multiphase chemical reactions. The mass transfer coefficient $K_{L,a}$, which determines the rate for gas-liquid absorption, was found to be in the range of 3-30 s$^{-1}$, which is at least 100 times better than in conventional reactors. The interfacial contact area, which is another measure of gas-liquid absorption capacity, was also experimentally determined to be as much as 100 times larger (as high as 16,000 m$^{-1}$) than in traditional gas-liquid contacting equipment. The cost for achieving such high levels of mass transfer comes in the form of the energy consumption or power dissipation (as reflected by the pressure drop). As was shown in section 8-3, the level of mass transfer is commensurate with the level of power dissipation. The microreactor is no less efficient than conventional reactors. The difference is that the microreactor allows one to achieve the higher levels of mass transfer which are unattainable any other way.

9.2.2. First micromachined packed-bed and novel gas-liquid contacting

Micromachining methods enable the efficient construction of complicated 2-dimensional extruded geometries. The microstructured reactor of chapters 6 and 7 is the first example of a completely micromachined packed bed reactor. The geometry, arrangement, and void fraction of the packing is determined precisely by the design of the reactor. This is in sharp contrast to the traditional approach of relying upon the random
arrangement of particles in a packed-bed format. As a result of defining the bed geometry, pressure drop and fluid distribution was controlled. As compared to gas-liquid contacting in open-channel capillaries, the microstructured channel promoted the mixing and dispersion of the two phases. The dispersed flow regime induced by the column arrays is unique to this system having never been observed in past gas-liquid flow studies. The increased level of interfacial contact area in this dispersed flow regime can have significant implications for improved heat and mass transfer for multiphase systems.

9.2.3. Comparison of integrated catalysts with conventional catalysts

The ability to precisely define the arrangement of the packed-bed is a positive feature of the microstructured reactors, but it requires the integration of the catalyst into the reactor. The reactor device is specific to a particular chemistry and modes of fabricating a particular catalyst may be proprietary or difficult to reproduce in a porous silicon substrate. The filter design of chapter 2 allows the integration of conventional catalytic materials (powders of high surface area catalysts) onto a chip-based format. The added advantage is that the catalyst can easily be removed and replaced with a different material for a different reaction or operation. In addition, the art of catalyst manufacture is left to those specialists who have a collective expertise spanning the last century of chemical production. By integrating the powdered catalysts onto the chip, formats for rapidly testing standard catalysts could become available. Novel semiconductor or MEMS-based chemical sensors could be coupled with the reactor in one package for higher sensitivity and faster operation.
9.3. Recommendations for Further Study

The multiphase systems investigated in this thesis were heterogeneously catalyzed gas-liquid reactions. There are abundant examples of other multiphase systems which would be equally suitable for microreaction technology, such as homogeneously catalyzed gas-liquid reactions or reactions between components in immiscible liquids, such as in phase-transfer catalysis. Other multiphase processes could benefit from novel devices available from the microfabrication methods presented here, such as extractions or emulsion formation. Examples of forming oil in water dispersions are presented in the next section.

For heterogeneously catalyzed gas-liquid reactions, the cyclohexene hydrogenation used as the model reaction in this thesis is a fairly simple chemistry. The lack of selectivity issues makes the analysis straightforward, but there is an opportunity for demonstrated an added feature to improved mass transfer: improving yield by controlling selectivity. Furthermore, the increased mass transfer could allow the successful investigation of intrinsic kinetics for a range of multiphase reactions.

9.3.1. Novel Materials by Microfluidic Synthesis

Whereas research in microchemical reactors to-date has focused on the synthesis of established commodity or specialty compounds, the area of novel material synthesis has yet to be explored. Microfluidic technology provides a number of unique advantages related to materials processing. With the improvements in heat and mass transfer resulting from higher surface-to-volume ratios, more control over the material forming process could lead to higher quality materials or materials with unique properties. An
example is in solids-forming processes where the particle size and the particle size distribution influence the properties of the material. Materials which have a strong relationship between particle morphology and function include drugs, pigments, and some semiconductors. Controlling the crystallization mechanisms of a pharmaceutical compound is recognized to have an important influence on therapeutic function. By directly controlling the interface, diffusion and contact time between two mixing streams, the microfluidic reactor may better direct the particulate forming process.

Figure 9-1. Oil droplet formation in water using the multichannel microreactor. (1wt% surfactant) A) Initial generation of oil droplets at the inlet channels. B) Continued growth of the oil droplets. C) Middle droplet breaks away and proceeds to flow down the channel. D) Droplets from adjacent channels cluster together.

An emerging area within microfluidics is the potential for control the processing of colloids and emulsions.[126] Modern semiconductor fabrication methods deal with features 0.1 μm in size; more practical MEMS devices will probably deal with features
closer to 1 μm. Nevertheless, reactors can be designed with characteristic length scales closer to those of the emulsions than in conventional reactors. Whereas in conventional processing the duration and speed of agitation may effect the emulsion's performance, micromixing devices could potentially gain wider control through manipulation of the dispersion process at the micro-level. Figure 9-1 contains a sequence of images showing the dispersion of an oil phase into water which contains 1 wt% surfactant (Triton-X). Without surfactant, the behavior is very different. Figure 9-2 illustrates the dispersion of oil in water showing the uniform distribution of droplet size within the channels of the microreactor.

![Microreactor Image]

**Figure 9-2. Oil droplet formation in water without surfactant.**

One such area of application for microfluidic emulsifiers could be in the microencapsulation of pharmaceutical agents for controlled delivery. Microfluidic reactors for creating emulsions could provide more control over the various parameters, such as size, morphology and size distribution of the polymer capsules. A microfluidic
platform could also more efficiently screen the various parameters (concentration of the polymer and protein solutions, organic/aqueous phases ratio). The other advantage to moving the encapsulation process to a chip is in the conservation of valuable therapeutic agents. The protein or compound involved may be in short supply: improving encapsulation efficiency and minimizing waste could be important benefits.

9.4. **Comments on the future.**

As 'chip' technology takes hold within analytical chemistry and modern computing becomes more sophisticated, chemical synthesis could one day become completely automated. Chip-based pumps, valves, and fluidic manifolds, currently under development in several labs, will one day automate all of the fluid manipulations carried out by hand today. Integrating these fluidic control elements with mixing units, reaction units, separation devices, and analytical devices will create multi-functional and rapidly configurable chemistry lab sets. All of the menial tasks now performed by chemists in the lab, such as the configuration of glassware, the transfer and mixing of reagents, the separation, purification, and analysis of products will one day be done at the computer terminal rather than the lab bench. The first applications have been for portable analytical equipment, but gradually the platforms are penetrating into traditional organic synthesis. Today, automated peptide synthesizers utilize sequences of automated chemical reactions that combine amino acids to create custom biomolecules. The future could hold a similar product for a much more diverse world of organic molecule synthesis.

The drive to such an automated, configurable microfluidics platform is the result of the inherent advantages of microfabrication and the benefits of engineering at the
microscale. Microfabrication holds the potential to mass fabricate identical chemistry lab components cheaply with a wide range of integrated functionality. Performing chemistry in the microscopic domain has the advantage of low reagent consumption, safety in terms of control and exposure, and improved process control due to superior heat and mass transfer.

The vision of integrating an entire chemical plant on a chip may be some time in coming, but the tools necessary to create an integrated, miniaturized chemical system are becoming more common-place. As the benefits of micro-scaled reaction devices become known, the drive to miniaturize will increase. This thesis has demonstrated, for a particular class of chemical reaction, that engineering features in the sub-millimeter regime can have a positive influence on the performance of the process. Microfabrication has also allowed us to re-think the way chemical reactors have traditionally been designed and has enabled the creation of entirely novel chemical reactors for multiphase chemical processes.
10. References


