Microfabricated Packed-Bed Reactor for Phosgene Synthesis

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A silicon micropacked-bed reactor for phosgene synthesis is demonstrated as an example of the potential for safe on-site/on-demand production of a hazardous compound. Complete conversion of chlorine is observed for both a 2:1 CO/Cl_2 feed at 4.5 std. cm^3/min and a 1:1 feed at 8 std. cm^3/min. The latter gives a projected productivity of ~ 100 kg/yr from a 10-channel microreactor, with the opportunity to produce significant quantities through operating many reactors in parallel. The versatility of silicon microfabrication technology for producing reactors for corrosive gases is demonstrated by a protective oxide coating formed during reactor fabrication. The increased heat and mass transfer inherent at the submillimeter reactor length scale provides a larger degree of safety, control, and suppression of gradients than is available in macroscale systems. These advantages are also explored in the extraction of chemical kinetics from microreactor experiments. The preexponential factor and apparent activation energy for phosgene formation are determined demonstrating the utility of micropacked-bed reactors as laboratory research tools.

Introduction

Microfabricated chemical systems are receiving an increased interest in a variety of chemical and biological applications. The microchemical research effort has grown as a natural extension of the expanding field of MicroElectroMechanical Systems (MEMS), which initially developed from integrated circuit fabrication technology. The miniaturization of chemical devices such as "micro-total-analysis-systems" (μTAS) is an example of this development (Van den Berg et al., 2000). Microchemical technology has also seen a broad range of development in a variety of unit operations such as heat exchangers, mixers, extractors, as well as chemical reactors (Ehrfeld et al., 1998; Jensen, 1999; Lowe et al., 2000). The ability to manufacture many reactors in parallel, analogous to computer chips in the microelectronics industry, also opens up the door for on-demand chemical synthesis (Lerou et al., 1995).

Silicon-based microchemical reaction systems with sub-millimeter length scales have the potential to realize systems with capabilities exceeding conventional macroscopic systems. The surface-area-to-volume ratio of the reaction channel increases as the characteristic length of the reactor is reduced. The larger area for heat transfer reduces thermal gradients, and, for exothermic processes, suppresses the formation of hot spots that otherwise could lead to reactor runaway. The ability to reduce runaway is not only an inherent safety advantage, but allows the reactor to be run under aggressive conditions or in regimes that would ordinarily be difficult or unsafe in larger systems. An example of this is ammonia par-

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tial oxidation with pure oxygen in a membrane-based microreactor (Franz et al., 1999; Srinivasan et al., 1997). Submillimeter length scales also enhance mixing, since the characteristic time of diffusion scales with the square of length. With characteristic diffusion times of milliseconds or less, mass-transfer gradients are also reduced.

Various microreactor designs have been fabricated utilizing thin film catalysts, coatings, or other structures (Janicke et al., 2000; Srinivasan et al., 1997; Weissmeier and Hönicke, 1998). These designs have small catalyst surface areas, and do not incorporate the broad range of catalyst supports and preparation techniques used in practice. A significant body of research and experience exists on catalyst development and synthesis. Leveraging this knowledge is desirable in implementing a catalytic microchemical platform. A micropacked-bed reactor has been demonstrated which utilizes high surface area catalyst particles (36–75 μm diameter) that are prepared with standard techniques (Losey et al., 2000). At these dimensions, the reactor operates in laminar flow at Reynolds numbers around unity for gas flows. In macroscale reactors (mm to m), low Reynolds numbers and larger catalyst diameters often lead to poor heat and mass transfer in packed beds due to the lack of turbulent mixing and slow diffusion over the larger length scales. The micropacked-bed dimensions, however, offset these deleterious transport effects and lead to more than a 100-fold increase in the gas-liquid mass-transfer coefficient relative to conventional systems for the multiphase hydrogenation of cyclohexene (Losey et al., 2001).

Economies of scale usually lead to large facilities from where chemicals are shipped. However, safety and environmental concerns could shift the current model towards smaller plants located near the intended point of application. This is particularly the case for hazardous and toxic chemical intermediates that have serious storage and shipping constraints. One such intermediate used throughout the chemical and pharmaceutical industry is phosgene ($COCl_2$, carbonyl dichloride), manufactured from gaseous chlorine and carbon monoxide over activated carbon

$$Cl_2 + CO \rightarrow COCl_2 \qquad -\Delta H = 26\ \text{kcal/mol} \tag{1}$$

The reaction is moderately fast and exothermic (Lord and Pritchard, 1970; Saunders et al., 1953).

Phosgene is widely used as a chemical intermediate for the production of isocyanates used in polyurethane foams and in the synthesis of pharmaceuticals and pesticides. Processes using phosgene require specialized cylinder storage, environmental enclosures, pipelines, fixtures under negative pressure, and significant preventative maintenance. Moreover, phosgene is under a variety of transportation restrictions. As a consequence, most phosgene is consumed at the point of production (EPA, 1985). 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 manufacturing of chemicals such as phosgene. Banks of reactors can be turned on or off as needed to maintain as close to zero stor-

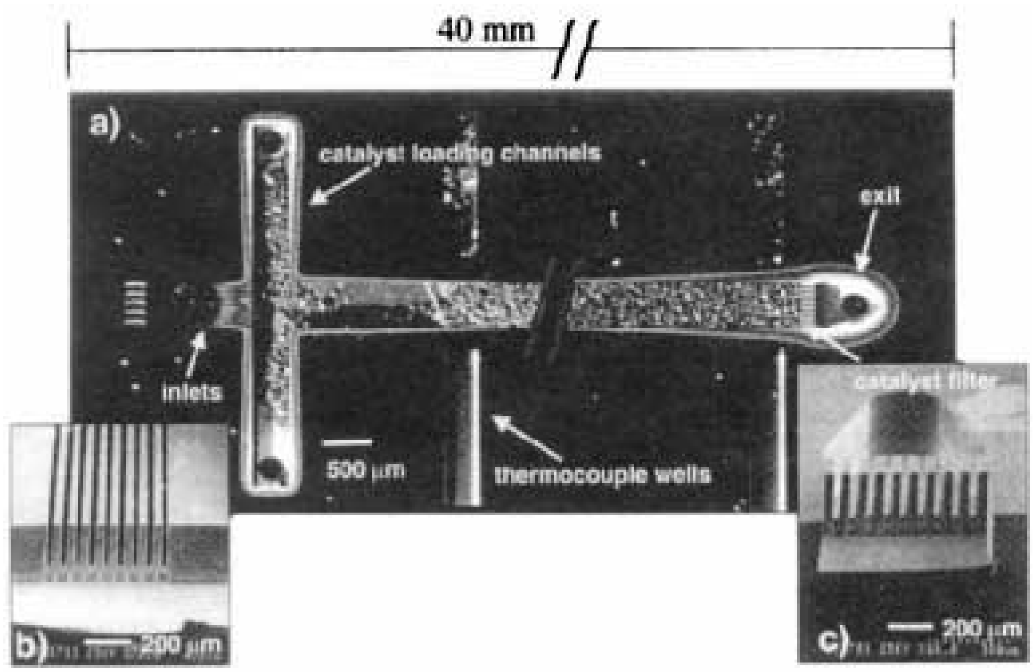

Figure 1. Microfabricated silicon packed-bed reactor.

(a) Top-view of reactor partially loaded with 60 μm activated carbon particles. The reactor channel is 20 mm long. The image is spliced to fit the 20 mm reaction channel by omitting the long channel midsection (photograph by Felice Frankel, MIT); (b) SEM of the 25 μm wide interleaved inlets; (c) SEM of the catalyst filter structure.

age as possible. Single reactor failures would lead to extremely small chemical releases. To demonstrate the ability to produce hazardous compounds from microfabricated devices, the DuPont Company has synthesized a number of hazardous chemicals such as isocyanates in a microreactor formed by bonded silicon layers (Lerou et al., 1995). Further, with the development of multistep microchemical systems, subsequent processing steps can be performed in a single device eliminating the need for storage or transportation.

In this work, we 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 preexponential factor and apparent activation energy for phosgene formation are determined to demonstrate the utility of micropacked-bed reactors as laboratory research tools.

Micropacked-Bed Reactor Design and Fabrication

A detailed description of the motivation, design issues, and characterization of the micropacked-bed reactor is described by Losey et al. (2001). The microreactor (Figure 1) is fabricated out of single crystal silicon with standard microfabrication processes developed for integrated circuits and MEMS. The geometry is defined using photolithography and created with silicon etching. The reactor consists of a 20 mm long, 625 μm wide, 300 μm deep reaction channel (3.75 μL volume) capped by Pyrex. Figure 1b shows a scanning electron micrograph (SEM) of the inlet where flow is split among several interleaved channels (25 μm wide) that meet at the entrance of the reaction channel. Perpendicular to the inlet channels are 400 μm wide loading channels used to deliver catalyst particles to the reactor. Catalyst is loaded by placing a vacuum at the exit of the reactor and drawing in particles through the loading channels. An inert gas can be used to load catalyst if contamination or deactivation is an issue. At the outlet of the reaction chamber, a series of posts with 25 μm gaps acts as a filter to retain the catalyst bed (Figure 1c). There are also four 325 μm wide channels perpendicular to the reaction channel along its length for holding thermocouples (or optical fibers). Access ports for flow come from underneath at the inlet (not shown in Figure 1), the reactor exit, and at the ends of the catalyst loading channels.

The thermocouple wells, inlets, the reactor and catalyst loading channels, and the catalyst filter are etched in a silicon substrate (100 mm diameter wafer, 500 μm thick) using a time-multiplexed inductively coupled plasma etch (Ayon et al., 1999). The wafer is then turned over, patterned, and etched on its back-side to create the access ports. Since chlorine etches silicon, a conformal silicon dioxide film about 5,000 Å thick is grown around the entire wafer in a wet oxidation furnace to protect the reactor. Finally, the oxide coated channels are capped by a Pyrex wafer (*Corning 7740*), which has a similar thermal coefficient of expansion as silicon, using an anodic bond (Schmidt, 1998). The bonded wafer stack is cut with a die saw to obtain individual devices. A 100 mm diameter wafer yields twelve single channel reactors (10 mm × 40 mm × 1.0 mm) after bonding and dicing.

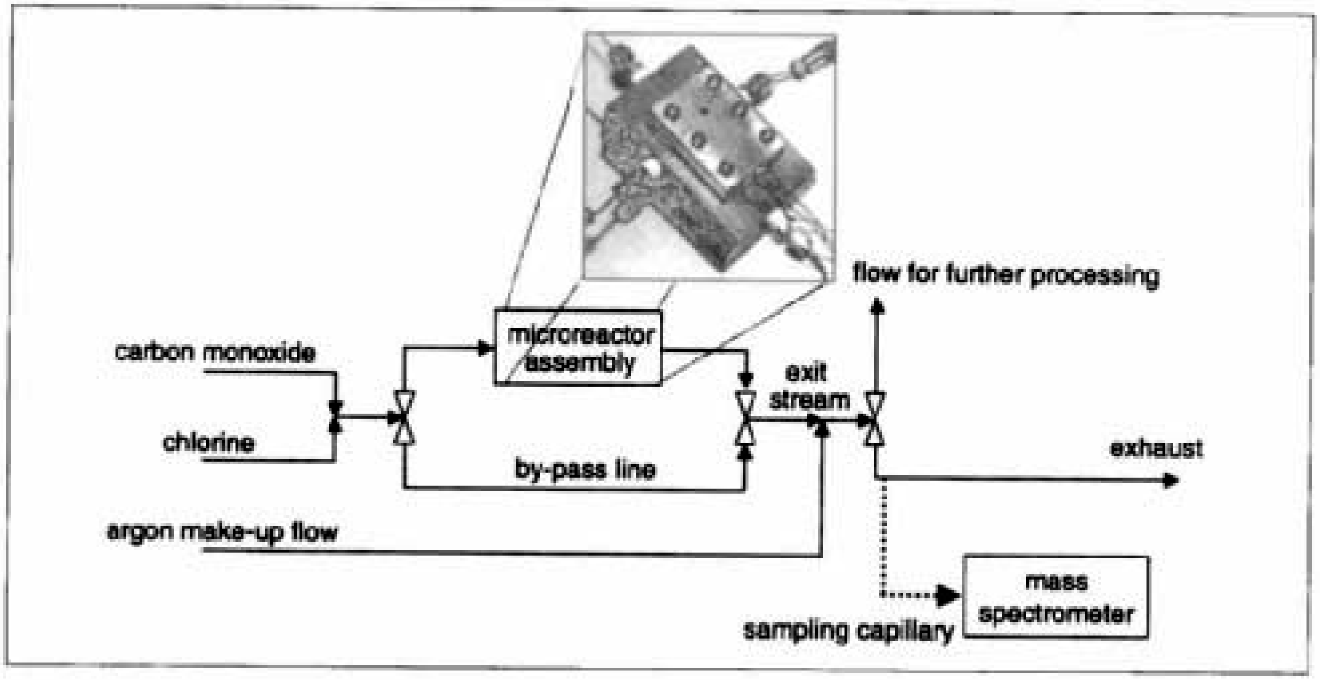

Figure 2. Experimental setup.

Flow controllers, purge lines, and other equipment have been eliminated for simplicity.

Experimental Setup

The reactor is compressed with a metal cover plate against a thin elastomer gasket (0.8 mm thick Kalrez) with punched through-holes to form fluidic connections to a stainless-steel base. External fluidic connections are made directly to the metal base (Figure 2). The metal compression plate contains cartridge heaters (*Omega Engineering*). Thermocouples (*Omega Engineering*) are threaded into the side wells of the reactor. Once the reactor is loaded with catalyst, the catalyst inlets are closed off by substituting a sealing gasket without catalyst loading through-holes.

The reactor/base assembly is connected to the rest of the system via standard fittings, valves, and 1.6 mm (1/16 in.) O.D. stainless-steel tubing. All materials in contact with chlorine, with the exception of the reactor, are stainless-steel, TEFLON, or Kalrez. The chlorine (*BOC Gases* > 99.96% purity) and carbon monoxide (*BOC Gases* > 99.3% purity) gas feeds are controlled by mass-flow controllers (*UNIT Instruments*). The carbon monoxide flow controller is specially fit with stainless-steel internal components. The chlorine flow controller is fitted with Kalrez fluidic seals to minimize degradation. The gas feeds are mixed in a tee junction, and enter either the reactor or a bypass line. The exit stream is interfaced via a glass capillary to a mass spectrometer pumped through a two-stage vacuum system for continuous real-time spectrometry. Any flow not drawn into the sampling capillary is directed to the exhaust, which is bubbled through a NaOH solution to remove any phosgene. The vacuum typically draws a larger flow through the capillary than the total flow rate used in these experiments. In order to prevent the difference from being drawn from the exhaust, argon purified in an oxygen and moisture scrubber is mixed with the exit stream just before the sampling capillary. The dry argon flow rate is adjusted with a mass-flow controller to make the total flow rate at the capillary inlet larger than the capillary draw rate. A switching valve is placed before the sampling capillary which either directs flow to the mass spectrometer as previously described, or to other laboratory equipment for further processing. High-pressure dry argon also serves as a purge gas at the beginning and end of the experiments. Before beginning an experiment, the entire system is heated to approximately 150°C for 2 h under a constant flow of dry argon. This removes adsorbed moisture which reacts with chlorine to form HCl and corrodes the setup. The entire system is inside a ventilated enclosure similar to a standard chemical fume hood. This highlights an inherent benefit of working with microreactors as additional safety structures and cooling mechanisms, which add expense and complexity to even typical laboratory work, are not needed.

The experiments were carried out with approximately 1.3 mg of activated carbon particles sieved between 53–73 μm with a surface area of 850 m^2/g (*DARCO G-60 American Norit Company*). The catalyst was loaded in air. A mixture of 2/3 CO and 1/3 Cl_2 was mixed at a total flow rate of 4.5 std. cm^3/min and fed into the reactor at room temperature. Some experiments were also done with a 50/50 stoichiometric feed at a total flow rate of 8.0 std. cm^3/min. The reactor was incrementally heated, without external cooling, from room temperature to approximately 220°C. The absolute pressure at the inlet of the reactor was approximately 1.35–1.40 atm (132 kPa) and was nominally atmospheric pressure at the exit.

Data Analysis

Data from the mass spectrometer are recorded on a PC with LABVIEW software (*National Instruments*). Since the exit stream is diluted with argon, post-run analysis is necessary to back out relevant partial pressures using calibrations performed at the beginning of each experiment. The calibration procedure involves flowing pure argon, chlorine, and carbon monoxide separately and in combination to the mass spectrometer and calibrating the intensities of the relevant mass fractions to the partial pressures of the respective species. Using the calibration, the partial pressure of argon is calculated at each data point during the experiment and is then used to scale the other mass fraction intensities (Millard, 1978). We decided not to calibrate the mass spectrometer using pure phosgene from an external gas cylinder because of the potential dangers and increased experimental complexity of having a pressured phosgene source. Instead, the calibration was done using phosgene produced in the microreactor at a complete conversion of chlorine. The overlapping mass fractions with chlorine (M/E = 70, M/E = 35) and carbon monoxide (M/E = 28) were deconvoluted by noting where the M/E = 70 chlorine mass fraction (minimal contribution from phosgene) stopped decreasing with increasing temperature. At this point, complete conversion of chlorine was assumed and the self-consistency of the calculations based on that assumption was examined.

At complete conversion, all mass fractions overlapping with chlorine can be calibrated. Stoichiometry and the mass fraction intensities of the excess CO can be used to calibrate the remaining phosgene mass fractions. Using the complete set of calibrations, the partial pressures of all three species were calculated for the entire data set. A correctly deconvoluted system gave the same value for conversion regardless of which of the three species the calculations were based. The conversion of chlorine (ξ_{Cl_2}) to phosgene was computed from the carbon monoxide, chlorine, and phosgene mol fractions using stoichiometric balances

$$\xi_{Cl_2} = \frac{x_{f_{Cl_2}}(1+Y)-1}{\left(x_{f_{Cl_2}}-1\right)} = \frac{\left(x_{f_{CO}}Y\right)+x_{f_{CO}}-Y}{\left(x_{f_{CO}}-1\right)} = \frac{x_{f_{COCl_2}}(1+Y)}{\left(x_{f_{COCl_2}}+1\right)} \qquad (2)$$

where x_{f_i} is the mol fraction of species i at the exit of the reactor, and Y is the ratio of CO/Cl_2 in the feed. Figure 3 shows the conversions computed independently from the three species over the entire temperature ramp from an experimental run. The consistency between the independently calculated values validates the original assumption of complete conversion made at the beginning of the data analysis and gives confidence to the data analysis procedure.

The equilibrium constant K_a for Reaction 1 confirms that full conversion is a reasonable assumption (Tester and Modell, 1997). Assuming an ideal vapor mixture at 450 K and 1.35 atmospheres (pressure at the reactor inlet), and using the heats of formation reported by Chase et al. (1985), the equilibrium constant indicates that a 2:1 mixture of carbon

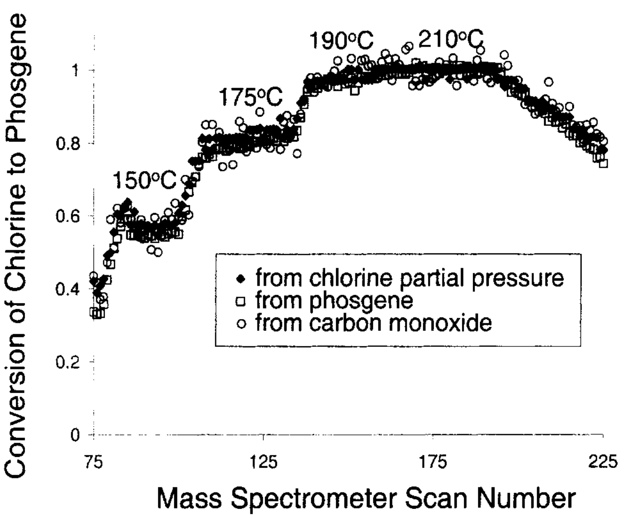

Figure 3. Conversion of chlorine to phosgene independently calculated from chlorine, phosgene, and carbon monoxide mass fractions.

The temperature was increased until complete conversion and then ramped down.

monoxide and chlorine would equilibrate at 99.99% conversion of chlorine. Complete conversion to the limits of detection was also reported by Shapatina et al. (1976).

Results and Discussion

Chemical compatibility

Chlorine etches silicon, particularly at elevated temperatures. Consequently, microreactors made from silicon would be corroded, releasing chlorine and possibly phosgene as well as losing the utility of defined features such as the inlets and catalyst retainers. Figure 4a shows the deleterious effects of exposing a silicon reactor to chlorine at 250°C. The reactor inlet and channel are severely etched. In contrast, the reactor with a silicon oxide coating (Figure 4b) shows no visible change after 6 h of continuous experiments. This example illustrates first, the importance of microfabricating chemically compatible systems, and, second, that even for systems where silicon is not suitable, thin chemically resistant coatings can be used to render a stable device.

Phosgene production

No temperature increase could be measured upon switching flow from the bypass line to the reactor. This 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. This gives fine temperature control over the exothermic reaction. No deactivation as reported by Shapatina et al. (1976) was observed during the experimental time-scales (6–10 h) possibly due to the high level of purity in the gas feeds. 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 were reacting with silicon, were also not detected.

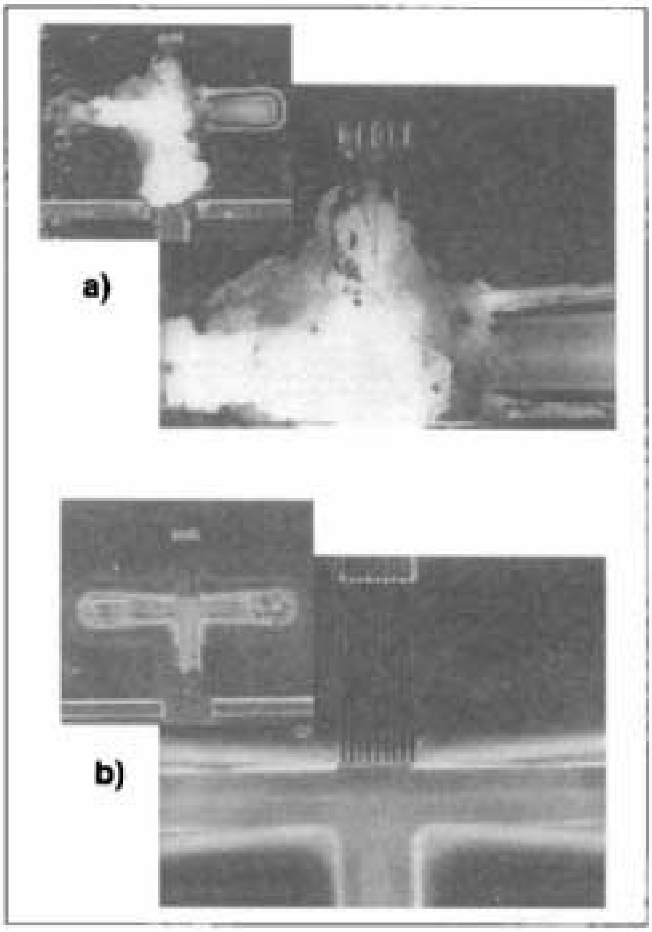

Figure 4. Protective coating of silicon dioxide prevents etching of the silicon reactor by chlorine.

(a) A microreactor etched catastrophically at the inlets under a constant 50/50 Cl_2/CO flow at elevated temperatures; (b) reactor protected with a conformal 5,000 Å oxide layer grown in a wet oxidation furnace. After high-temperature-flow for over 6 h, the reactor shows no noticeable degradation.

Figure 5 shows the average conversion of chlorine to phosgene as a function of temperature. The conversion of chlorine peaks at about 200°C where it stops increasing with increasing temperature. Using the rationale described in the data analysis, it was confirmed that the tailing off was not a result of mass-transfer limitations, but from complete conversion. At 4.5 std. cm^3/min total feed rate with 33.3% chlorine, a phosgene productivity of 3.5 kg/yr (0.40 g/h) is projected for a continuously operating single channel device. Experiments were also done with an 8 std. cm^3/min stoichiometric feed. Complete conversion to phosgene was observed with a corresponding phosgene productivity of 9.3 kg/yr (1.1 g/h). The flow rates were not increased due to the limitations of the mass-flow controllers, but the ability to control thermal runaway in these microsystems would safely allow an aggres-

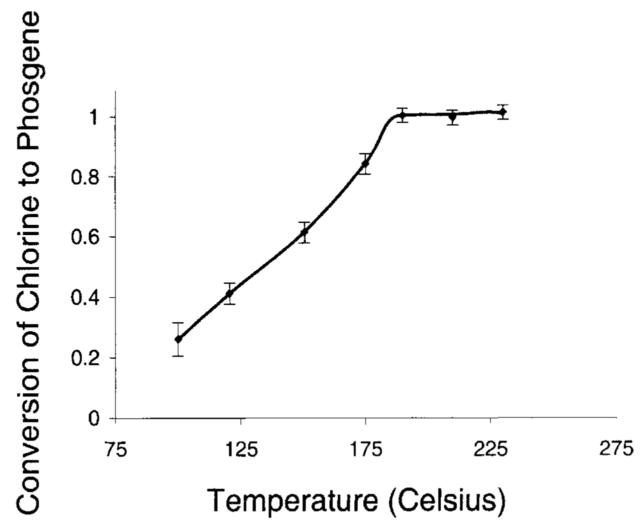

Figure 5. Conversion of chlorine with a 1:2 chlorine/carbon monoxide feed at 4.5 std. cm³/min total flow rate.

Complete conversion is seen at approximately 200°C giving a projected productivity of 3.5 kg/yr (0.40 g/h) of phosgene from the single channel reactor.

sive increase in temperature and flow rate into ordinarily dangerous regimes, further increasing productivity. A multichannel reactor integrating 10 reaction channels with a common inlet and exit onto a single chip has been fabricated and is only 1.5×larger in total chip area (Losey et al., 2001). Experiments with other systems show that the productivity of the multichannel microreactor scales with the number of integrated channels. A single 10-channel device would produce 93 kg/yr (11 g/h) of phosgene with an 80 std. cm³/min stoichiometric feed at the given temperatures. Again, the opportunity to increase temperature and flow rate exists. Scaling out with multiple devices operating in parallel would provide additional opportunity to produce substantial amounts of phosgene in an on-demand fashion.

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 (Othmer, 1982). Following a procedure for the synthesis of cyclohexylisocyanate (Sheehan et al., 1961), 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 50 mL 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.

Extraction of kinetics from the microreactor system

The small dimensions reduce thermal gradients that otherwise would complicate the determination of reaction kinetics from packed-bed reactor data. In order to demonstrate the microreactor as a tool for measuring reaction kinetics, rate constants for phosgene formation were extracted assuming plug-flow (PFR). The PFR assumption is reasonable based on the reactor Peclet number. Calculated values range between 180 and 360. The number of catalyst particles across the reactor diameter is ~6.4, whereas a value of 10 or more is typically desired for plug-flow analysis. In order to examine further the potential for gradients in the packed bed, characteristic dimensionless numbers were considered on the basis of experimental data.

Anderson (1963) proposed a criterion for assuring that the observed reaction rate does not differ from the actual reaction rate within a catalyst particle by more than 5% due to intraparticle temperature gradients

$$\frac{|\Delta H|\, R_{rxn} r_p^2 E_{\mathrm{act}}}{k_p T_s (RT)} < 0.75 \tag{3}$$

The carbon catalyst in the phosgene experiments may be considered isothermal as the lefthand side of the inequality ranges between ~0.0006–0.006 using experimental data and a thermal conductivity of ~0.27 W/m·K for porous activated carbon (Satterfield, 1996). The Weisz modulus M_w, which gives the ratio of the reaction rate to the diffusion rate in the porous catalyst is

$$M_w = \frac{R_{rxn} r_p^2 \rho_p}{C_s D_E} \tag{4}$$

BET nitrogen adsorption and specifications from the catalyst manufacturer indicate that Knudsen diffusion effects are important. With a calculated effective diffusivity ~10^{-7}m²/s, the Weisz modulus was determined to be between 0.1–0.5 indicating minimal intraparticle mass-transfer limitations, even with the low diffusivity.

In traditional packed beds, low particle Reynolds numbers typically result in poor mass transfer to the catalyst particle surface. Relationships have been developed for the Sherwood number in packed beds governing mass transfer from the fluid film around a particle to the particle surface (Kunii and Suzuki, 1967; Satterfield, 1970; Wakao and Tanisho, 1974). Their applicability to microfabricated reactors where diffusive mixing is fast is unclear. However, an order of magnitude analysis can be made by examining the concentration gradient needed to maintain a flux corresponding to reactant consumption at the largest reaction rate observed in the experiments. In the limiting case of mass transfer, where Reynolds number approaches zero, diffusion is the only form of transport to the catalyst surface. For a 63 micron particle at the fastest rates of phosgene formation observed in the experiments, the concentration difference is calculated to be approximately 0.01 mol/m³ over a characteristic length of one particle diameter. This is negligible compared to the bulk concentration of ~15 mol/m³. Therefore, mass transfer to the catalyst surface is not limiting and the reactant concentrations at the catalyst surface may be taken as the same as the bulk concentrations. Furthermore, the interstitial diffusion time from one particle to another (taken as 1 particle diameter) is on the same order as the single particle residence time based on the superficial velocity of the gases, that is, $Pe_{\text{particle}} \sim 1$. The preceding analyses demonstrate how the small microreactor length scale reduces heat- and mass-transfer gradients in packed beds. Since characteristic thermal and mass transport times decrease as a square of the characteristic length, the micropacked-bed reactor operates in a regime where diffusive mixing and heat transfer across the small catalyst pellets are fast enough to suppress gradients.

The PFR equation material balance

$$F_{i_o} d\xi_i = -r_i dW \tag{5}$$

is integrated, where F_{i_o} is the flow rate of species i in mol/time at the reactor inlet, ξ_i is the conversion of species i, r_i is the rate of formation/consumption of species i, and W is the mass of catalyst. The rate of reaction (mol/s/g catalyst) is taken from a rate expression reported by Shapatina et al. (1976)

$$R_{rxn} = kP_{\text{CO}}\left(\frac{P_{\text{Cl}_2}}{AP_{\text{CO}} + P_{\text{COCl}_2}}\right)^{1/4} \tag{6}$$

where k is the Arrhenius rate constant (mol/s/atm/g catalyst), P_i is the partial pressure (atm) of species i, and the constant A is a temperature-dependent equilibrium constant. This expression was obtained from experiments performed between 70–130°C. The temperatures in this analysis extend to 180°C, and Eq. 6 is extrapolated outside the range reported by Shapatina et al. for both data analysis and comparison. Equation 6 only applies to regions of intermediate CO surface coverage occurring at chlorine mol fractions above 3% (Shapatina and Kuchaev, 1980). As chlorine partial pressure decreases, the reaction passes from a region of intermediate surface coverage to a region of high coverage where the catalyst is almost completely covered by adsorbed CO. The expression in Eq. 6 does not capture this change in surface characteristic. Low chlorine concentrations occur in the micropacked-bed reactor towards the exit of the reactor at high conversions. Therefore, Eq. 6 was only used to obtain kinetics below 80% chlorine conversion to ensure that the chlorine mol fraction was always above 3%.

The Ergun equation (Eq. 7) is often used to describe the pressure drop in traditional packed beds (Bird et al., 1960)

$$\frac{dP}{dL} = -\frac{G}{\rho D_p}\left(\frac{1-\phi}{\phi^3}\right)\left[\frac{150(1-\phi)\mu}{D_p} + 1.75G\right] \tag{7}$$

Experiments measuring the pressure drop through the micropacked bed were performed using nitrogen (0–20 std. cm^3/min). Equation 7 was integrated assuming a compressible gas, and the void fraction (ϕ) was determined to be approximately 0.4 by fitting the data using ϕ as the only variable parameter. Using the determined ϕ, the Ergun equation gives a good prediction of the pressure drop for the range of gas flow studied in the phosgene experiments, justifying its use in further analysis.

The reduction in the total number of moles in Reaction 1 causes the density of the gas stream to increase with conversion. This causes a nonlinear decrease in total pressure along the reactor channel. Substituting Eq. 2 and an expression for density as a function of conversion into Eq. 7, the pressure drop along the reactor channel with respect to catalyst weight can be written as

$$\frac{dP}{dW} = -\frac{G}{\sigma_c \rho_0 D_p}\left(\frac{1-\phi}{\phi^3}\right)\left[\frac{150(1-\phi)\mu}{D_p} + 1.75G\right] \times \frac{P_0}{P}\left(1 + \epsilon\xi_{\text{Cl}_2}\right) \tag{8}$$

where P is the total pressure at any point along the reactor, W is the weight of catalyst along the reactor, σ_C is the catalyst packing density in terms of the weight per unit length along the reactor channel (kg catalyst/m channel), ϵ is the % change in the number of moles at complete conversion, as defined by Fogler (1992), and ξ_{Cl_2} is the conversion of limiting reagent (chlorine) along the reactor. $\epsilon = -1/3$ for the case of a 2:1 CO/Cl$_2$ feed. The viscosity of the gas mixture is assumed to be constant for this analysis. Plugging Eqs. 2 and 6 into Eq. 5, the conversion of chlorine along the reactor with respect to catalyst weight is

$$\frac{d\xi_{\text{Cl}_2}}{dW} = k\left(\frac{Y - \xi_{\text{Cl}_2}}{Y + 1 - \xi_{\text{Cl}_2}}\right)\left(\frac{1 - \xi_{\text{Cl}_2}}{A\left(Y - \xi_{\text{Cl}_2}\right) + \xi_{\text{Cl}_2}}\right)^{1/4} \frac{P}{F_{\text{Cl}_2 o}} \tag{9}$$

Equations 8 and 9 together give a system of coupled differential equations in both P and ξ for which all the parameters are known except the rate constant k. Values for k were extracted by iteratively solving the coupled system at different temperatures using a fourth-order Runge-Kutta algorithm (Hoffman, 1992) with the constraint that conversion at the exit of the reactor matches the data shown in Figure 5. Using BET measurements on the catalytic surface area, the rate constants with respect to surface area are calculated and compared to values from Shapatina et al. in Figure 6. The experimental error bars are calculated using statistical analysis on the repeatability of the data at 95% confidence. Shapatina et al. (1976) reported catalyst surface area before and after each experiment. The post reaction surface area is used in Figure 6. A reasonable agreement is seen between the experimental values and the values reported by Shapatina et al. given that they did not report error analysis and that this analysis extrapolated their expressions outside of their reported temperature range. The apparent activation energy from the experiments of 7.6 kcal/mol compares with the 8.6 kcal/mol reported by Shapatina et al. 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.

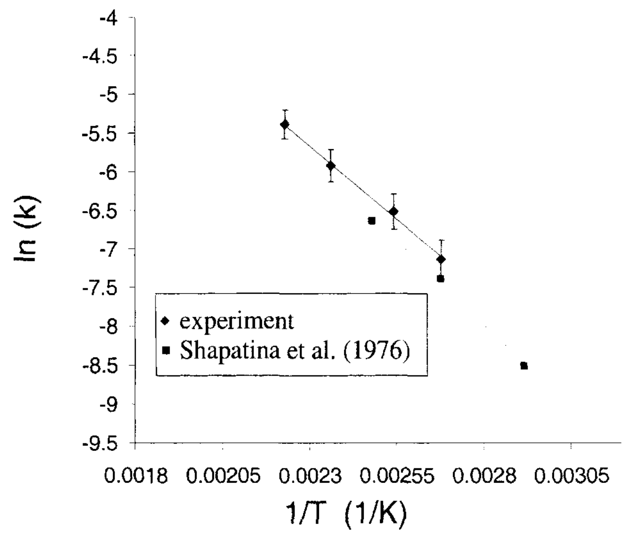

Figure 6. ln (k) vs. 1/T for the phosgene experiments and Shapatina et al. (1976).

The experimental activation energy of 7.6 kcal/mol compares favorably to 8.6 kcal/mol from Shapatina et al.

Conclusions

A silicon-based micropacked-bed reactor has been presented for the heterogeneous gas-phase production of phosgene. The microreactor utilizes high surface area catalyst particles synthesized by standard procedures. By using catalyst particles instead of thin-films or coatings, current industrial catalysts can be utilized for a wide range of applications. An example of the robustness of microfabrication technology for chemical processing is demonstrated through the use of a silicon-dioxide layer to protect the reactor from chemical attack.

Phosgene production was used as an example of the potential for safe on-site/on-demand production of a hazardous compound. The production of phosgene, normally requiring significant investment in infrastructure, was easily performed in a standard ventilated enclosure. Even with test-tube scale reactors, catalyst temperature control and thermal gradients are difficult to control. With toxic compounds such as phosgene, a bank of these "macroscale" reactors for catalyst testing would require special enclosures and expensive safety precautions. In contrast, a bank of microreactors would offer minimal structural investment beyond a small ventilated enclosure or fume hood while providing fine temperature control and reduction of both thermal and concentration gradients.

Preliminary productivity values for a single reaction channel device yielded 9.3 kg/yr (1.1 g/h) of phosgene for an 8 std. cm^3/min stoichiometric feed of carbon monoxide and chlorine. Although the flow rates were not increased due to limitations in the mass-flow controllers, opportunity exists for increasing productivity as temperature and flow rates can be aggressively increased without compromising safety. A multichannel device integrating 10 reaction channels onto a single chip has been fabricated that would increase productivity by a factor of ten. A scaled-out system with multiple parallel ten-channel reactors could yield substantial amounts of phosgene. Bench-scale synthesis of an isocyanate from an amine with phosgene produced in the microreactor was demonstrated. Although only performed in a 50 mL flask, temperature control was an issue as significant temperature excursions were noted when external cooling was not applied. These excursions negatively impact selectivity and are an example of the difficulty of thermal control with these types of reactions on the industrial scale. Future work involves integrating the microreactor producing phosgene with a second microreactor designed for gas-liquid contacting. The complete microchemical system would perform both the phosgene production and the subsequent phosgenation, eliminating safety issues with handling phosgene and enhancing control over selectivity. The suppression of hot spots and increased mass-transfer capabilities were also explored as advantages for the extraction of chemical kinetics. Quantitative analysis indicates that the catalyst particles are small enough to be isothermal and that mass-transfer resistances are not severe for the phosgene experiments. Rate constants for phosgene formation were extracted from the packed-bed data and compared favorably with literature, demonstrating the potential for micropacked-bed reactors as practical laboratory research tools.

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Notation

C_s = concentration of limiting reactant at the catalyst surface, mol/m^3
D_p = diameter of catalyst particle, m
E_{act}/RT = Arrhenius group (activation energy, universal gas constant, temperature)
G = superficial mass velocity, kg/(m^2·s)
ΔH = change in enthalpy of forward reaction, J/g mol
k_p = catalyst thermal conductivity, W/m·K
P_o = measured pressure at the inlet of the reactor, atm
r_p = catalyst particle radius, m
T_s = catalyst surface temperature taken as the bulk fluid temperature, K
ρ_f = fluid or gas density, kg/m^3
ρ_p = catalyst density, kg/m^3
μ_i = viscosity of species i, Pa·s

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