Silicon Based Microreactors

Klavs F. Jensen

Departments of Chemical Engineering and Materials Science and Engineering
Massachusetts Institute of Technology
77 Massachusetts Avenue
Cambridge, MA 02139

The microscale revolution in chemistry promises to transform classical batch wise laboratory procedures into integrated systems capable of providing new understanding of fundamental chemical processes as well as rapid, continuous discovery and development of new products with less use of resources and waste generation. Applications of silicon based microreactors are illustrated with a broad range of cases studies, including high throughpunt experimentation in organic synthesis, integration of ultraviolet (UV), visible and infrared (IR) spectroscopy; investigations of high temperature heterogeneous catalytic reactions, obtaining high mass transfer rates in gas-liquid reactions over solid catalysts, enabling difficult to perform reactions, synthesis of solid nanoparticles, and high temperature conversion of hydrocarbons to hydrogen.
Introduction

The term “microreactor” originally referred to small tubular reactors used in catalysis research, but with advances in microreaction technology it has become synonymous with microfabricated systems consisting of multiple sub-millimeter channels in which fluid flows continuously and chemical reactions take place (1-12). These microreactors have the potential for less waste, fewer utilities, higher throughput experimentation, and safety advantages compared to conventional reaction systems. The small reaction volumes of microsystems combined with the high heat and mass transfer rates enable reactions to be performed under more aggressive conditions with higher yields than can typically be achieved with conventional reactors. Moreover, new reaction pathways deemed too difficult to control in conventional macroscopic equipment can be conducted safely because of the high heat transfer and ease of confining small volume. The latter feature becomes particularly important when chemical transformations involve highly reactive intermediates. In that case, large exotherms can lead to thermal runaway with potentially catastrophic consequences. These inherent safety characteristics of microreactors also imply that systems of multiple microreactors could be deployed in distributed point-of-use synthesis of small volume chemicals with storage and shipping limitations, such as highly reactive and toxic intermediates.

Microreaction technology is closely related to integration of analytical tools as in the field of micro Total Analysis (µTAS) systems (13-16). In fact, when microreactors are integrated with chemical analysis, such as optical spectroscopy, they become powerful tools for determining chemical kinetics and optimal conditions for chemical reactions. Microreactors with larger sized channels (~mm) become useful in process intensification—a field that often employs ceramics monoliths as “multichannel microreactors”.

A microreactor based process can, in principle, be scaled to meet demands for product testing by multiplying the numbers of reaction chips and running the reaction for longer times. This “scale-out” strategy, as opposed to the traditional “scale-up,” makes it feasible to go from microgram to kilogram quantities without additional chemistry modifications or reactor engineering. Furthermore, the use of a continuous processing technology instead of batch wise synthesis eliminates batch-to-batch variation and enables tight control of product specifications. Microreactors can also be used to accelerate conventional scale-up by more rapidly providing essential chemical mechanics and kinetic information than conventional pilot plant experimental facilities. The ultimate choice between scale-up and scale-out depends on the chemical kinetics, heat transfer characteristics, and production levels of the process.

The choice of design and construction material for a microreactor depends on the intended application. Classical chemical reaction engineering principles (18,19) apply to microreactor design and prediction of performance. A large number of microreactor designs have been realized in stainless steel (1-3,8,20), glass (9,10), silicon (7), and polymers (21). Additional examples of microreactor studies appear in this volume.

Stainless steel microreactors have typically been used in microreactor
applications relevant to chemical production, whereas glass reactors have been attractive for laboratory applications, in part because of the chemist’s traditional use of glass equipment. Microreactors realized by rapid prototyping in poly(dimethylsiloxane) (PDMS) (21) have been used extensively in biochemical studies because of the rapid turn-around from design to experiment offered by this platform. However, limited chemical compatibility, low mechanical strength, and low thermal conductivity typically restrict applications of the technique for non-aqueous and elevated pressure/temperature systems.

Silicon is also a useful material for realizing microreactor designs. The large fabrication infrastructure developed for microelectromechanical systems (MEMS) (22) provides a series of integrated fabrication platforms for producing complex, three-dimensional microchannel networks. Well established wet and drying etching procedures (23,24) enable fabrication of microchannels with controlled sidewall shape and channel dimensions from nm to mm. Moreover, advances in silicon microsensors, e.g., flow, pressure, and temperature sensors, can readily be integrated with the microreactors. Silicon has excellent mechanical strength and temperature characteristics, and it has good chemical compatibility characteristics. Oxidation of silicon leads to the formation of a glass layer on the surface so that an oxidized silicon microreactor becomes functionally equivalent to a glass reactor. For cases where silicon or glass lacks the necessary chemical resistance, such as for fluorination reactions, it is possible to deposit protective coatings (25).

In this contribution, we illustrate the use of silicon based microreactors for (i) high throughput experimentation of homogeneous organic synthesis, (ii) integration of ultraviolet (UV), visible and infrared (IR) spectroscopy; (iii) investigations of high temperature heterogeneous catalytic reactions, (iv) obtaining high mass transfer rates in gas-liquid reactions over solid catalysts, (v) enabling difficult to perform reactions, (vi) synthesis of solid nanoparticles, and (vii) high temperature conversion of hydrocarbons to hydrogen. The need for integration of reaction units with fluid control, separation, and analytical techniques is also briefly discussed.

High Throughput Experiments

The glycosylation reaction shown in Figure 1a serves as an example of probing the reaction space with microreactors (26). When combined with a suitable analytical technique, in this case high performance liquid chromatography (HPLC) with an auto-sampler, microreactors can be used to scan through reaction space to optimize reaction conditions and to gain understanding of reaction mechanisms and rates. Characteristic of complex organic transformations, glycosylation is often a difficult synthesis, which depends on the chemical nature of the reaction partners as well as reaction variables such as composition, temperature, reaction time, and activator (27,28). Much effort in organic synthesis is spent on searching for optimal reaction conditions to achieve a particular transformation. Moreover, method optimization can ultimately require significant time and large quantities of valuable starting materials. Thus, microreactor based techniques for efficiently
identifying optimal reaction conditions could have major impact on research and development in organic chemistry.

Figure 1. Example of glycosylation reaction. (a) microreactor designed to perform the glycosylation reaction (b), and results (c) (26)

The five-port silicon microreactor (Figure 1b) exemplifies microreactor design components typically need to realize a particular organic transformation. It has a mixing region providing controlled contact of the reactants – in this case, glycosylating agent, nucleophile (acceptor), and activator – in such a manner that side reactions are minimized. Lamination of reaction streams by narrow channels is sufficient for the present case. Increased mixing could be achieved by incorporating one of the many microfluidic mixing schemes demonstrated over the past decade (29), e.g. chaotic advection through patterned channel walls (30). In general, the mixer should be designed to have a mixing time significantly shorter than the reaction time. Once mixed, the reactants enter the reaction zone which provides sufficient residence time for the reaction to proceed. A simple channel typically suffices for homogenous reactions, whereas flow obstacles in the channel (“packaging”) is useful to increase interfacial area in heterogeneous reactions (see below). If the Peclet number (defined as $UL/D$, where $U$ is the flow velocity, $L$ is the characteristic length of the channel, and $D$ is the diffusivity of the reactants),
where $U$ is the average velocity of the liquid, $L$ is a characteristic dimension and $D$ is the diffusion coefficient) is high, advection dominates over diffusion and the time a flow segment spends traveling through the channel will equal the reaction time.

A quench port is included near the outlet, so that the reaction can be quenched before the reaction stream exits the reactor for collection and analysis. This port is important in quantitative work with microreactors, since the outlet tubing otherwise adds a significant volume and uncertainty as to whether the reaction was completed in the device or the reactor interface to the macroscopic fluid handling environment.

Results from the microreactor-HPLC case study show a clear relationship between reaction temperature, reaction time and formation of product (Figure 1c). For a given reaction time, the yield of product increases with temperature until maximum conversion is achieved. At temperatures lower than the optimum, yield increases with increasing reaction time (i.e., decreasing flow rate). Moreover, the formation of orthoester, a major side product, is observed at lower temperatures. The example demonstrates the ability of the microreactor system to rapidly obtain comprehensive information about a given transformation. With a single preparation of reagents, 44 reactions were completed in less than a day at varying temperatures and reaction times requiring just over 2 mg of glycosylating agent for each reaction. Conventional batch reaction procedures would have been limited to ~3 experiments/day and have required significantly larger quantities of starting material.

**Integration of IR Spectroscopy and Microreactors**

Integration of chemical analysis methods and physical sensors (e.g., temperature and pressure) enhances the utility of microreactors for optimization as well as studies of reaction mechanisms and kinetics. Integrated chemical sensors offer the potential for computer control optimization of reaction conditions, which reduces the time and materials costs in identifying optimal operating conditions. Miniaturized chemical analysis systems have been developed for the most macroscopic counterparts (14-16). Specific techniques for monitoring species concentration include fluorescence, electrochemical, optical absorption (UV-vis and IR), and nuclear magnetic resonance (NMR) methods. The availability of excellent optical fibers, light sources, and detectors in the UV-vis to near IR makes it possible to integrate these techniques in microreactors (31,32). If absorption bands are easily distinguished, these techniques can be useful for monitoring species, but the broad nature of the absorption bands means that it is difficult to obtain sufficient information for detailed chemical studies.

Fourier transform infrared spectroscopy (FTIR) methods are efficient, broadly applicable techniques for determining chemical structure and quantifying species concentrations. As a result, FTIR has been implemented in microsystems by a variety of approaches, including capping microchannel structures with IR transparent materials and integrating microreactors with off-chip FTIR detection (33-35). Silicon is transparent to IR radiation in most of the
wavelength region of interest (4000-800 cm⁻¹). The thin SiO₂ that could be formed by oxidation to increase chemical compatibility is still sufficiently thin (~500 nm) to not impact the IR transmission characteristics of the device. In fact, for transmission studies, dielectric coatings of silicon oxide and nitride can be used to reduce reflections and improve transmission through the reactor (36). Figure 2 shows a silicon based microreactor combining micro mixing, a reaction channel, an IR detection region, and temperature control along with measured NaOH absorbance at different levels of concentrations (36). As an example of the utility of monitor concentrations, the reactor was used to determine the rate constant for alkaline hydrolysis of methyl formate.

The strong IR absorption of many solvents, especially water and suspensions, limits the path length in solution through which the incident IR radiation can travel. In that case, sampling by the evicine wave at the interface

![Microreactor with mixer, heat exchanger, and transmission FTIR section (a). Data obtained monitoring hydroxide, small contributions from interference patterns are apparent in the absorption peaks (b) (36).](image-url)
between the solution and an Attenuated Total Reflection (ATR) (also called Multiple Internal Reflection, or MIR) crystal (Figure 3a) becomes an attractive method for FTIR spectroscopy (37). Anisotropic etching of silicon provides a simple alternative to commercial crystals produced by individually polishing crystals, which makes them expensive and difficult to integrate. Moreover the microfabricated crystal can be integrated into microreactors to produce integrated systems for monitoring the progress of a particular reaction, as exemplified in Figure 3b for the model reaction system, hydrolysis of ethyl acetate.

For gas phase reactions, the short path lengths in microreactors and low optical densities of gases typically render IR absorption spectroscopy impracticable in gas-phase microreactors. Photoacoustic spectroscopy (PAS) is a potential alternative optical method for gas-phase detection (38,39). In this technique, incident light is modulated at an acoustic frequency and if the optical wavelength couples to an energy transition in the gas, the gas absorbs the light resulting in a periodic gas expansion. The small thermal mass of microreactors, especially membrane based systems (40), and the ability to measure pressure fluctuations (as in hearing aids) implies that the techniques could be implemented in microreactors. PAS applies to many chemical compounds and its sensitivity scales inversely with dimensions. The microreactors with integrated gas sensing have been demonstrated, but several technical issues have
Microreactors for Heterogeneous Catalytic Reactions

The interest in faster development of new catalysts has led to significant advances in high-throughput screening and combinatorial methods in which large arrays of catalysts are rapidly screened. Detailed characterization of catalyst performance, such as kinetics, selectivity, and deactivation, is necessary for translation of promising candidates into process environments. These studies are simplified by the use of a reactor in which mass, thermal, and pressure gradients are minimal, but the realization of such conditions can be a challenge with traditional reactor technology. Microfabrication of chemical reactors, such as micro packed-beds, provide unique advantages for the efficient testing of catalysts, including reduced transport limitations and increased surface area-to-volume ratio for enhanced heat transfer. Microfabrication also gives flexible control over reactor geometry enabling configurations difficult to realize in macroscopic testing systems.

Conventional catalyst testing is typically performed with small tubular reactors. A corresponding, microfabricated packed-bed channel reactor (Figure 4a) with 60 µm catalyst particles demonstrates the potential for using microfabricated reactors to obtain chemical kinetics (41). However, this configuration has significant pressure drop due to the small catalyst particle size. In general, low pressure drops and small conversions (differential operation) facilitates obtaining chemical kinetics for catalyst testing experiments. On the other hand, it is desirable to have as much catalyst as possible for subsequent analysis of the catalyst (42). Microfabrication enables a solution to these apparent contradicting demands in the form of a silicon-based, cross-flow packed-bed, microreactor for catalyst testing (Figure 4b) (43). This design integrates short parallel beds into a continuous wide packed-bed, providing for short contact time with sufficient catalyst to allow characterization of reaction performance and catalyst post-reaction structure. Even flow distribution across the wide bed is accomplished by 256 shallow channels that provide a pressure drop much larger than the pressure drop through the catalyst bed. In this way, differences in catalyst packing density have negligible effect on the overall flow distribution. The cross-flow geometry renders the bed isothermal and isobaric. Moreover, the cross-flow geometry enables the use of practical flow rates and catalyst quantities while minimizing pressure drop.
The operation of the cross-flow microreactor was characterized through finite element simulations and experiments with model catalytic reactions—CO oxidation and ethyne hydrogenation on supported catalysts \((43,45)\). The consistency of kinetic parameters (turnover frequency and activation energy) and mechanistic information (reaction order) obtained in the microreactor with...
previously reported values across different catalysts, demonstrated the potential of microfabricated cross-flow reactors as laboratory tools for heterogeneous catalyst testing. A quantitative analysis of the transport effects in the microreactor showed that the small catalyst particle size and reactor geometry eliminate mass and thermal gradients both internal and external to the catalyst particles. By reducing thermal, mass, and pressure gradients and ensuring even flow distribution over the catalyst bed, the cross-flow microreactor provides a useful platform for the determination of kinetic parameters.

**High Mass Transfer Rate Multiphase Microreactors**

For fast multiphase reactions, the rate and selectivity of the chemical process can be greatly influenced by the transport of reagents within and across phases. Using silicon microfabrication, it is possible to construct packed-bed microreactors (Figure 5) that provide a hundredfold or more improvement in mass transfer for gas–liquid heterogeneously catalyzed processes, such as hydrogenation of unsaturated hydrocarbons (44). In these devices, standard catalyst particles (50–75 µm diameters) are retained in silicon channels by an integrated microfabricated filter unit. A specially designed gas-liquid inlet section with narrow channels provides rapid contact of the gas and liquid reagents. In order to achieve uniform flow, pressure drops in the inlet gas and liquid sections exceed those in the individual reactor channels.
Figure 5. Multiphase-multichannel microreactor - with porous catalyst particles (a) or microstructured packing (b) (44,46).

The small particles provide the high surface areas for improved gas–liquid mixing, but they also represent a challenge in terms of pressure drop and fluid distribution among the ten parallel channels. The pressure drop can be reduced by replacing the catalysts bed by a microfabricated support structure, such as illustrated in Figure 5b (46). In this case, the catalyst support consists of arrays of columns, 50 µm in diameter, 300 µm tall, with nearly 20,000 columns per device. As a result of the extreme uniformity of the structured packing arrangement, control over fluid flow is greatly enhanced relative to the micro packed-beds. The columns are microfabricated by using deep reactive ion etch (DRIE) technology (23) and the challenge becomes to incorporate the catalyst in such a manner that the activity is comparable to that of the standard catalysts. The activity is greatly enhanced if the catalytic component is supported upon a porous layer, formed by making the silicon posts porous (46,47), or by forming a porous alumina wash coat (48). The resulting surfaces can be impregnated with noble metal catalyst by standard catalyst preparation techniques, or homogeneous catalysts could be immobilized on the surfaces by using linking
techniques recently demonstrated for glass channel reactors (49).

**Microreactors for Difficult to Perform Reactions**

The high heat transfer rates and small reactor hold-up volumes associated with microreactors, make it possible to perform reactions that are difficult to perform in large conventional reactors. As an example, Figure 6a (50) shows data from direct synthesis of hydrogen peroxide from hydrogen and oxygen in a dilute sulfuric acid/phosphoric acid/sodium bromide solution flowing over palladium catalysts at 30 atm pressure in a multiphase microreactor similar to that shown in Figure 5. By keeping the bubble size small and having excellent gas-liquid contact with the solid catalysts, the heterogeneous reactions are preferred over homogeneous reactions that could lead to chain branching free radical reactions and ultimately, explosion. Thus, it becomes feasible to directly synthesize hydrogen peroxide from mixtures of hydrogen and oxygen in the explosive regime.

Oxidation of olefins by ozone is another example of a useful reaction (51) that can be difficult to run in conventional reactors because of the high heat of reaction and the potential for highly reactive side product formations, e.g., peroxi-polymers (52,53). However, it has the advantages of high selectivity and generation of oxygen as the only side product. The high-surface-to-volume ratio in microreactors increases the gas-liquid interface area enhancing mass flux of ozone through the interface, and facilitates removal of heat generated by the chemical reactions. Including microfabricated post structures in the channel (Figure 6b) increases further interfacial area and mixing in the reactor. Ozonolysis of olefins and amines at room temperature led to very high conversion (>98%) and selectivity, even at short contact times <1s (54).
Figure 6. Data from direct formation of hydrogen peroxide from hydrogen and oxygen reacting at 30 atm over a carbon supported palladium catalyst in a microreactor similar to Figure 5 (a) (50, 54). Multiphase multichannel microreactor with posts used in ozonolysis, panels show details (b) (54).

The direct fluorination of organic reagents is yet another example of a transformation rarely practiced on a preparative scale because of the difficulties in controlling the large heat of reaction and the selectivity of the process (25). Moreover, because of the low solubility of fluorine in commonly used solvents, reactions tend to proceed at the gas-liquid interface and form localized hot spots.
Thus, direct fluorination forms an excellent case for microreaction technology, and it has consequently been demonstrated in several different reactor types(55,56), including silicon-based microreactors (25). In order to make the latter reactors chemically compatible, a nickel surface coating was included. Direct fluorination has also served as an inspiration for development of flow distribution, allowing controlled scaling of gas-liquid reactions from a few channels to a large number of channels (~100) with uniform flow distribution (57,58). This flow distribution can be measured by integrated flow sensors (Figure 7), which use multiple optical waveguides to monitor flow regimes and detect the speed of liquid segments (plugs) moving through different channels (59).

Figure 7. Photograph of a multichannel, multilayer ("numbered -up") microreactor for gas-liquid reactions, specifically direct fluorination. The metal lines form optical wave guides for the flow sensor (57-59).

Synthesis of Solid Particles in Microreactors

Generation of solid particles is generally thought to be a problem for microreactors in terms of agglomeration and plugging of channels. Nevertheless, with carefully control of nucleation and growth, microreactors can be an excellent tool for continuous synthesis of particles with well-controlled properties. This is particularly the case for nano-sized particles requiring multiple synthetic steps, such as synthesis of colloid particles and subsequent surface modifications for biological assays and optics (60,61).

Scaling down dimensions to sub-millimeter in a microreactor provides opportunities for improved size and composition control of colloidal synthesis. Microfabrication also affords increased flexibility in reactor design; specifically,
reactant-contacting schemes difficult to achieve in macroscale units can be realized. Simple homogeneous flow is not usually desirable for particle synthesis in microreactors because of broadening of the size distribution by axial dispersion—the variation in residence times caused by the fluid moving slower near the tube wall than in the center. The dispersion effect can be reduced and a narrow particle size obtained by using a segmented flow in which the synthesis fluid is divided into separate fluid segments (plugs) moving through the channel as small individual batch reactors. The segmenting fluid, aside from dividing the synthesis liquid into small batches, also serves to accelerate micromixing by recirculation within each segment. Gas-liquid segmented microreactors are attractive by the ease with which the gas can be separated from the liquid by using capillary forces (62).

Synthesis of colloidal silica by the Stöber method (63), an extensively studied system, serves as a model system. Figure 8a illustrates a microreactor, fabricated in PDMS, which has sufficient chemical compatibility to handle the water-ethanol -tetraethoxy silane mixtures used in this case. The synthesis of silica is characterized by rapid initial growth followed by slow growth, which implies that synthesis in a single phase flow will be particularly sensitive to residence time effects at short times. Particles near the wall move slower than those near the center of the channel, and thus spend more time in the reactor. On the other hand, in the segmented flow the synthesis fluid is divided into a series of well mixed batch reactors (Figure 8b), which produce a narrow size distribution (Figure 8c). These results illustrate the importance of being able to quantify, the residence time distribution (RTD) of each fluid element in the microreactor. Measurement of the RTD is readily accomplished in microreactors, by introducing a means for injecting a fluorescent tracer (e.g., by using an integrated piezoelectric bending disk element) and then following the spatial spread of the fluorescence as the tracer plug flows through the channel (64).

![Figure 8. Microreactor for synthesis of colloidal silica particles (a), schematic of a gas-liquid segmented flow (b), and representative sample of silica particles synthesized in the microreactor (c) (60).](image)

The synthesis of nanocrystalline, semiconductor quantum dots (QDs) (2-10
nm diameter), specifically CdSe, constitutes a second example of microreactor facilitated particle synthesis (61). The optical properties and average size of QDs synthesized in conventional batch processes are influenced by factors that are difficult to control such as injection process, local temperature and concentration fluctuations, rate of stirring, and rate of cooling. A gas-liquid segmented flow microreactor allows for rapid and controlled mixing of precursors. Moreover, as in the case of colloidal silica, the segmented flow narrows the RTD and thus, the size distribution of QDs produced. Silicon is used as the material of construction to allow nucleation and growth at temperatures up to ~300ºC, which are needed to achieve good luminescence properties of the QDs. The silicon is again oxidized to provide the glass surface preferred in many chemical applications.

**Microreactors for High Temperature Fuel Conversion**

Microreactors for high temperature conversions of hydrocarbon fuels to thermal energy and hydrogen constitutes the last illustration of the advantages afforded by silicon technology in realizing microreactors designed for specific applications. There is considerable interest in miniaturizing conversion of hydrocarbon fuels to electric power generation for portable applications since combustible fuels store up to a hundred times more energy per unit weight than batteries. However, fuel conversion systems have proven difficult to miniaturize because of a number of challenges, perhaps most importantly, thermal losses. Thermal loss to the environment caused by the rapid heat transfer across small devices is a major problem for any miniaturized system involving one or more high-temperature steps, such as combustion engines, thermoelectric (TE) and thermophotovoltaic (TPV) generators, and fuel cell systems based on high-temperature fuel processors for hydrogen production.

Figure 9 shows a suspended-tube reactor that directly addresses the thermal management issues in small fuel processors (48). This microfuel processor consists of four thin-walled (~2 µm) silicon nitride tubes (~300 µm hydraulic diameter), comprising two separate U-shaped fluid channels. On one end, the tubes are fixed into a silicon substrate containing fluidic channels and ports; on the other end, the channels form a free-standing structure. This free end (hot zone) is partially encased in silicon to form a thermally isolated silicon region in which the chemical reactions take place. Heat conduction along the length of the tubes is very small due to the high aspect ratio (2 µm wall thickness, 3 mm length) and low thermal conductivity of the silicon nitride tubes. The tubes contain silicon slabs that permit heat transfer between fluid streams (for heat recuperation) without significantly adding to heat loss down the length of the tubes. In the case of hydrogen production (e.g., ammonia cracking or hydrocarbon reforming), combustion in one stream provides the energy required for endothermic reforming in the other stream. The high thermal conductivity of the silicon in the reaction zone improves the heat transfer between the two process streams. In TPV applications, the thermally isolated silicon zone would serve as a nearly isothermal fuel combustor that radiates to a photovoltaic cell (TPV) (65). The microcombustor could also have applications in high temperature, short contact chemistry.
The suspended-tube reactor has additional features, including a thin-film heater and temperature-sensing resistor, and internal structures within the tubes and silicon reaction zone, and passive stop valves. The thin-film heater is used to initiate and/or carry out chemical reactions, while the temperature sensors are for control. The internal structure increases heat transfer characteristics and the catalyst surface area achievable using catalyst washcoats (48).

The suspended tube design efficiently isolates a high-temperature zone and maintains a temperature gradient of greater than 2000°C/mm while simultaneously minimizing heat loss to the environment. The device can be used to produce hydrogen from a variety of fuels, with a projected hydrogen production of > 1 W per reactor. In the case of hydrocarbon reforming, the produced hydrogen would contain small amounts of carbon monoxide, which would have to be removed before using the hydrogen in a fuel cell. The hydrogen could be removed by using microfabricated palladium membrane purification devices (66).

**Conclusion**

The above examples selected from the MIT effort represent a small fraction of the variety of designs for microreactors being pursued at many academic institutions and company research laboratories. Examples of those efforts are given elsewhere in the volume and in the referenced literature. Future evolution of microreaction technology will require combining separation with microreactors to enable multi-step synthesis. Progress has been made in microfluidic systems for both gas-liquid separation (62) and liquid-liquid extraction (67), but general multi-step synthesis procedures remain a challenge.
The necessity of synthesizing sufficient quantities for subsequent evaluation dictates that microchemical systems are operated as continuous systems. Such systems will need fluid controls for adjusting reagent volumes and isolating defective units. Integration of sensors will enable optimization of reaction conditions, as well as the extraction of mechanistic and kinetic information. Early implementation of integrated microchemical systems is likely to involve modular systems with microreactors, separation units, and analytic components mounted on electrical, fluidic, and optical “circuit boards” (68) (see Figure 10).

The realization of integrated microchemical systems ultimately will revolutionize research by providing flexible tools for rapid screening of reaction pathways, catalysts, and materials synthesis procedures, as well as faster routes to new products and optimal operating conditions. Moreover, such microsystems for chemical will clearly require less space, use fewer resources, produce less waste, and offer safety advantages. Progress towards integrated systems will require continued development and characterization of microreactors, separation units, and integrated analytical methods, as well as new, innovative approaches for connecting modular microfluidic components into flexible fluidic networks allowing active control and providing potential for matching components to a particular application.

Figure 10. Conceptual picture of integrated microreactor system (a). Example of early stage microreactor “Circuit board” (68,69)

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