Flexible Microreactor System for Chemical Research at Moderate Temperatures

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ABSTRACT

Miniaturization is fast gaining attention in chemical processes that are conventionally carried out on a lab-scale or larger. Major progress and landmarks have been made during the last five years. A microreactor system has been developed for fast catalyst development and process optimization. This paper focuses on the issues of microreactor system design and characterization for fast and accurate reaction analysis.

1. INTRODUCTION

The advancement in silicon micromachining and precision technology has made the miniaturization in chemical process very attractive in reaction characterization, catalyst development, process optimization, etc [1]. Microreactors are well suited as laboratory reactors because of the many advantages they possess, mostly because of their small size [2, 3, 4]. Their microscale dimensions result in ultra-low transport resistances with the result that the transfer of heat [5] and the diffusion of mass [6] are extremely quick giving these devices an agility of operation. Extremely expensive or rare chemical systems can be economically explored because of the low reactant species consumption [7]. The small footprint of the microreactor and its peripherals (controllers and analytical instruments) implies that less infrastructure is needed for operation, including floor space, energy, and support personnel. In addition, these microfabricated reactors have the potential to be integrated with sensors and controllers [8], reducing the need for outside peripherals. These technical advantages are achieved with the added benefit that the small reactant volumes are highly safe, being nearly exempt from explosion even when operating in what would normally be considered explosive regimes [8]. Moreover, the environmental hazards due to leakage are minimal.

The microreactors designed and fabricated were based on state-of-the-art silicon micromachining techniques. They were then characterized in an experimental setup that allowed the reacting gases to pass through the reactor and the effluents to be analyzed by a mass spectrometer (MS) or a Gas Chromatograph (GC)/MS system. The setup included the tubing system with flow and pressure control and a reactor interface block with temperature control using electric heater and cooling water. This single microreactor system is further expanded to a microkinetic array with the ability of simultaneous analysis of multiple reactors, by the use of two electronically controlled multiposition valves (Figure 1) [9, 10, 11, 12].

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Figure 1: Schematic of Microkinetic Array: flow control is through mass flow controllers; pressure control is obtained with a feedback control of inlet/outlet pressure gauges and downstream pressure controllers; by using multiposition valves, one GC/MS system can analyze multiple reactors simultaneously.

2. MICROREACTOR DESIGN AND CATALYST INCORPORATION

The microreactors, comprised of channels etched in a silicon substrate were fabricated using well-known silicon bulk micromachining techniques involving photolithography and etching [13]. There are two kinds of microreactors fabricated with different channel dimensions, as shown in Figure 2. Gas inlets and outlets located in the end areas, with the channel area (reaction zone) located in the center.

Figure 2: Photos of two microreactors fabricated in this work: (A) The reactor has tens to hundreds of straight microchannels 100 µm x 100 µm in cross-section or microchannels 5 µm wide and up to 250 µm deep. (B) This reactor has hundreds of zigzag microchannels 5 µm x 100 µm in cross-section, with more channels and larger reaction area compared to (A).

Catalysts can be deposited in the microchannels by a variety of methods based on thin-film technology [14], traditional catalyst preparation [15], and other new methods [2], [9].
3. SYSTEM DESIGN AND AUTOMATION

The microreactors were characterized and analyzed using the experimental setup described in Figure 1. Reaction conditions of each microreactor, including reactant flow rates, temperature, and pressure, were controlled individually [16, 17]. Through a self-developed LabVIEW™ program, both control and data acquisition was automated. A MS was employed to gather reactant and product information, and hence to study reaction details such as conversion, selectivity, rate law, etc.

While the reaction was conducted in the microreactor, the reactor chip interfaced to a steel interface block fitted with o-ring sealed gas connections to the inlet and outlet openings on the bottom side of the chip. Resistive heating elements, cooling water channels and thermocouples were equipped in the block for temperature control. Gases were fed to the block by mass flow controllers and digital pressure sensors are situated in the inlet and outlet streams so that pressure could be monitored and further controlled by the additional usage of a pressure controller at the downstream of the system. The outlet stream for the experiments was then split at atmospheric pressure. Most of the stream was sent to the exhaust with the rest sent to a MS or GC/MS system for reaction analysis.

A single microreactor system without the multiposition valves was used in all experiments conducted previously [18]. A microkinetic array for multiple reaction analysis is being developed with the integration of two multiposition valves. The valve in immediate connection with the pressure controllers is a Valco™ 16-port 16-position flow-through valve. The valve can be electronically controlled to switch between different microreactors, by sending effluent from an individual reactor to the second multiposition valve each time. Sixteen-position implies sixteen microreactors can be analyzed in a multiplex fashion with a single gas analyzer (MS, GC/MS). The second multiposition valve is a Valco™ 8-port 2-position valve, which can be equipped with sample loops with different volumes. An inert carrier gas is used to feed the reactor effluent to the gas analyzer (GC/MS) and to prevent cross contamination between different reactor effluents.

4. REACTOR INTERFACE BLOCK DESIGN

One of the crucial elements in the experimental setup was the reactor interface block, responsible for seamless connection between the tubing system and the microreactor (Figure 3). The major concern in the block design was the isolation of reaction stream from the atmosphere and precise reaction temperature control. Silicone o-rings were used for reactor inlet and outlet sealing. Small brackets (not shown) held down the reactor against the o-rings so that hermeticity was attained.

Most of the reactions we studied demanded elevated temperatures (from 50°C to 500°C). While the channel area (reaction zone) was heated to elevated temperatures, the inlet and outlet area required lower temperature operation because of the low melting point of the silicone o-rings (about 200°C). Cooling water channels were introduced for this purpose. Both ANSYS™ thermal modeling (not shown) and experiments (Figure 4) substantiated the ideal thermal distribution for the block center (uniform high temperature) and block ends (<200°C).
5. REACTION ANALYSIS WITH MS AND GC/MS

The procedure for quantitative analysis of the reaction effluent began by calibrating the MS with ambient air as a standard for establishing the sensitivity to nitrogen. Pure reactant and products were flowed in the reactor in combination with nitrogen in order to determine their respective sensitivity factors [19, 20]. Further calibration is crucial for quantitative analysis because the overall sensitivity of MS is influenced by different gas concentrations. Especially the existence of species with low ionization energy (hydrogen, for example) in the gas mixture will enhance sensitivities for all gases at different levels, which results in the inaccurate partial pressure readings in MS [21]. The calibrated MS was then used to record continuous partial pressure data during the course of experiments where conditions of temperature and reactant flow rates were varied. A new analysis method using GC/MS is under development for more accurate and complete analysis.

Different model reactions have been studied in our microreactor system, including hydrocarbon hydrogenation/dehydrogenation, hydrocarbon oxidation, methanation, etc. Please refer to [2], [3], [9] for more details.

6. CONCLUSION

This paper summarizes the work on the design, characterization and analysis of a microreactor system. It emphasizes the system automation including flow, temperature and pressure control, and the reactor interface block design to gain a desirable thermal distribution. Reactor fabrication and reaction analysis are also introduced.

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