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Development of a microreactor-based parallel catalyst analysis system for synthesis gas conversion

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Abstract

This paper presents the development of a microreactor-based parallel-analysis system for fast catalyst development. The method is based on the deployment of multiple, microfabricated chemical reactors which consume little energy or chemicals, are safe and environmentally compatible in operation, and which yield relevant reaction data for catalyst evaluation. The approach is a general one, applicable to various heterogeneous catalysis technologies. The aim of this research is to ultimately apply the method to Fischer–Tropsch (F–T) and other syntheses related to the production of non-petroleum based fuels and chemicals. Because of the large gains in experimental efficiency, the method has the ability to advance catalyst technology at an unprecedented pace.

We begin by describing our previous work involving the fabrication of silicon micromachined microreactors and the mechanical and electrical setup for the experimental characterization of microreactors. We then present the results of a model reaction system (hydrogenation and dehydrogenation of cyclohexene) and preliminary results of methanation reactions performed with this setup. Finally, the parallel-analysis system, which is currently under development, is discussed.

Keywords: Microreactor; Combinatorial; Synthesis gas conversion; Fischer–Tropsch; Methanation; Cyclohexene hydrogenation and dehydrogenation

1. Introduction

Starting from pharmaceutical research with respect to the identification and optimization of drugs, combinatorial methods for synthesis and screening have become increasingly important for other chemical and biological species as well, e.g. regarding homogeneous or heterogeneous catalysts or other types of materials [1]. There are generally two approaches to combinatorial catalyst screening developed among different research groups: (1) high sample throughput with less information gained on each sample [2,3] and (2) lower sample count with more complete information obtained on each sample [2,4], depending on the candidate preparation and screening techniques. The first approach normally pursues a large number of candidates (>100) to extract ten or so “leads” based on relatively limited screening information. In contrast, the second approach, which collects more detailed reaction information for a group of leads, then facilitates the further elimination of less effective candidates from this group. In addition, the approach also yields information useful for process scaling and deployment in actual industrial processes. Based on the second combinatorial screening approach and coupled with our experience with microfabricated

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reactor (microreactor) research, we are developing a microreactor-based parallel catalyst-analysis system for industrially important reactions to dramatically decrease the catalyst development period and reduce overall operating costs.

During the last 2 decades, Fischer–Tropsch (F–T) synthesis, being the technology for conversion of natural gas to liquid and as an attractive alternative for bringing static gas resources to market, has been re-visited by several entities including Exxon-Mobil, Shell, Sasol, Syntroleum, Rentech, etc. and commercialized by Shell, Sasol, etc. Among these companies and other research groups, extensive interest has been focused on finding a better catalyst to increase productivity, to control hydrocarbon product distribution and to lengthen the catalyst life [5,6]. The idea of using a parallel-analysis system as a fast, economic and easy-to-scale-up solution for F–T catalyst development, fits these requirements appropriately.

A microreactor system based on modern silicon micromachining techniques, state of the art precision engineering and automation can provide a complete solution for fast F–T catalyst development [7]. Microreactors are well suited as novel laboratory reactors because of the many advantages they possess, namely, high transport rates, low reactant consumption, low infrastructure requirements, personnel safety, and environmental compatibility. Their microscale dimensions result in ultra-low transport resistances such that the transfer of heat and the diffusion of mass are extremely quick giving these devices an agility of operation so that they equilibrate nearly instantaneously both thermally and compositionally. They consume reactant species only very slowly, with the effect that extremely expensive or rare chemical systems can be economically explored. The small footprint of the microreactor and its peripherals need less infrastructure for operation, including floor space, energy supply, and support personnel. This compactness also allows an experimental approach whereby an array of microreactors are connected to share flow and analysis equipment, allowing a number of catalyst analysis experiments to be performed in parallel, increasing experiment throughput and reducing development time. These technical advantages are achieved with 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. Moreover, the environmental hazards due to leakage are minimal. Our research group has successfully proved the applicability of this system by analyzing a model hydrocarbon hydrogenation/dehydrogenation in the above system [7,8].

Catalyst preparation methods are a major concern in catalyst development since both catalyst component composition and nanostructure strongly influence the outcome. The microreactor is compatible with a number of catalyst preparation techniques, including physical vapor deposition (co-sputtering and sequential sputtering), sol–gel techniques, nanoparticle self-assembly, and impregnation methods. An ultimate goal is to integrate catalyst synthesis methods relevant for F–T technology, including precipitation-based methods, and to have precise control of catalyst composition and structure in the microreactor.

2. Microreactor fabrication and experimental setup

The microreactors we have used are 1 cm × 3 cm silicon chips with anodically bonded Pyrex covers, as shown in Fig. 1. Silicon is chosen as the reactor material because of its ease in processing, based on well-known fabrication from micro-electro-mechanical system (MEMS) technology. For this application, silicon is a versatile material, possessing mechanical robustness, chemical inertness, and high thermal conductivity. Inlets and outlets at the ends of chip connect to the catalyst-coated channel reaction area. This reaction area has channels of either 5 μm width (800 in number) or 100 μm width (40 in number) and 50–100 μm depth, with surface-to-volume ratio dramatically higher than conventional laboratory reactors.

The microreactor experimental setup is built to seamlessly connect microreactors with inlet and outlet flows. Reactant flow rates, reaction pressure and temperature are automatically controlled through LabVIEW$^{\text{TM}}$ in the setup. A mass spectrometer is employed to gather reactant and product information, hence to study reaction details like conversion, selectivity, rate law, etc. Control of process parameters and acquisition of reaction data are automated [7].

Various catalysts can be deposited in the microchannels by different methods based on thin-film

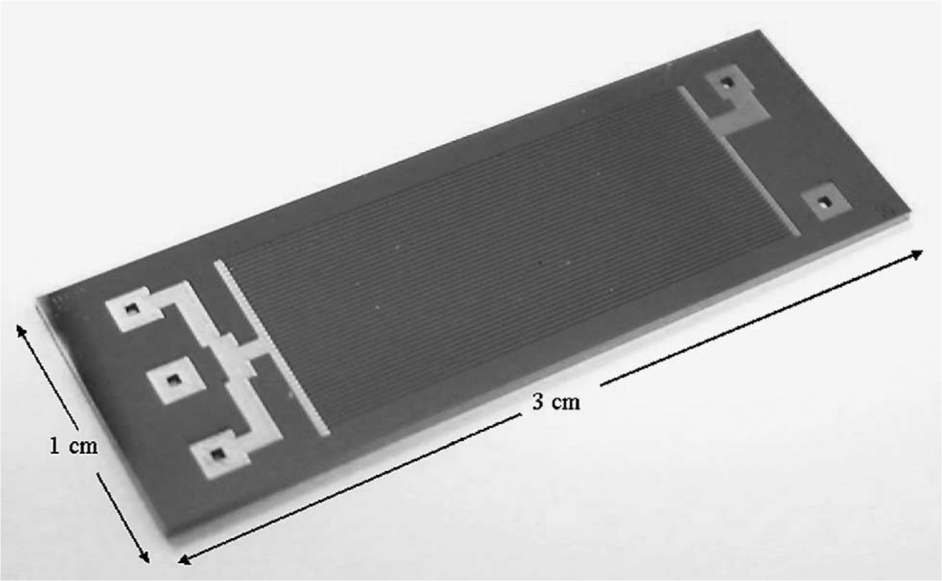

Fig. 1. Microreactor fabricated by our group and used in the study.

technology [9], traditional catalyst preparation [10], and other new means. Thin-film methods include vacuum sputtering [11], vacuum evaporation [12], and chemical vapor deposition [13]. Traditional catalyst preparation methods include sol–gel deposition [14] and impregnation [15]. Other techniques based on surface modification methods such as electrodeposition [16], anodization [17], electroetching [18] or even nanoscale construction techniques like deposition of nanoparticles [19], have been adopted recently.

The catalysts (Pt, Fe, Co) used in the experiments described here were deposited with vacuum sputtering of high-purity (>99.99%) metallic Pt, Fe or Co directly onto the bare silicon surface. A shadow mask was incorporated during deposition to block unwanted Pt/Fe/Co flux from the periphery of the top surface of the silicon reactor chip where the anodic bonding interface was to subsequently be formed. Each catalyst film had a nominal thickness of 20 nm, and had a smooth and unremarkable appearance in SEM images. The films were not porous and no surface area enhancement occurred through deposition. Therefore the total catalyst surface area could be closely estimated by a simple geometrical calculation of the microchannel area in the reaction zone. Subsequent to catalyst deposition, the reactors were subjected to a thermal treatment during the anodic bonding process used to attach the Pyrex cover to the reactor. During this step, the reactor was heated to 450 °C in air for 45 min.

3. Results

We have explored two model reaction systems using this setup. The hydrogenation and dehydrogenation reactions of cyclohexene over platinum catalyst have been characterized for conversion, selectivity, space-time yield, and reaction probability in several different reactors having both 5 and 100 μm microchannels [7,8]. Exploration of synthesis gas (syngas) conversion in the microscale has begun and initial data have been obtained for CO/H_2 methanation using an iron catalyst. As stated before, the catalyst preparation procedures for both reactions are nominally identical.

3.1. Cyclohexene hydrogenation and dehydrogenation

Cyclohexene hydrogenation/dehydrogenation (Eqs. (1) and (2)) is representative of important hydrotreating and reforming reactions ubiquitous in the

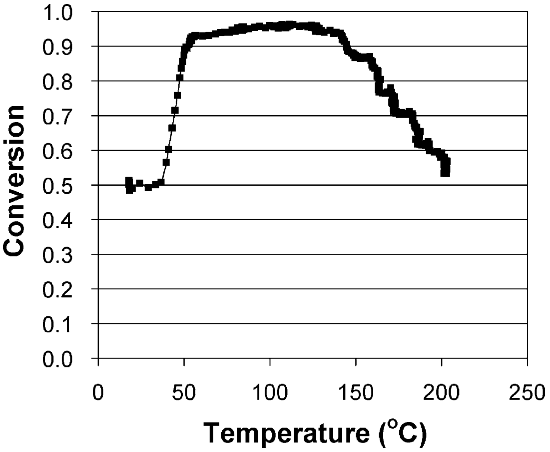

Fig. 2. Cyclohexene conversion vs. temperature: flow(H_2) = 0.3 sccm, flow(C_6H_{10}) = 0.1 sccm; 1 atm pressure.

petroleum refining industry [20]. The characterization results for several 5 μm/100 μm (width) × 100 μm (depth) chips are summarized in Figs. 2 and 3. The catalysts in these devices were prepared identically through vacuum sputtering of Pt. The flat, 20 nm-thick films had a total surface area of 2.2 cm^2 (100 μm-width reactors) or 31 cm^2 (5 μm-width reactors). This sputtering process is known to result in films of reproducible thickness, density and microstructure [9]. The reactors were then pretreated with pure H_2 flow (1.0 sccm) at 20 °C for 90 min.

$$C_6H_{10} + H_2 \xrightarrow{Pt} C_6H_{12} \quad (1)$$

$$C_6H_{10} \xrightarrow{Pt} C_6H_6 + 2H_2 \quad (2)$$

Fig. 2 shows the study of catalyst activity at different temperatures. The initial conversion transient indicates the catalyst is immediately active for conversion of the cyclohexene reactant at room temperature. After a temperature of about 120 °C is reached, catalyst activity is strongly correlated to temperature in that a significant decline occurs because of the deactivation of Pt catalyst above 120 °C [21]. The effect of residence time on reaction conversion is shows in Fig. 3(a). The conversion was found to be a strong function of residence time in 100 μm-width chips where it changed from about 15% at a minimum to about 80% maximum. But in 5 μm-width chips the change in conversion was small, which is due to the fact that 5 μm-width chips have an increased surface area, which accommodates the increase in flow rate and hence the decrease in residence time does not bring about a large change in conversion. In Fig. 3(b), selectivities of both 100 μm-width and 5 μm-width chips show strong dependence on temperature. This shift in selectivity at higher temperatures is due to the changing catalytic surface conditions [22,23].

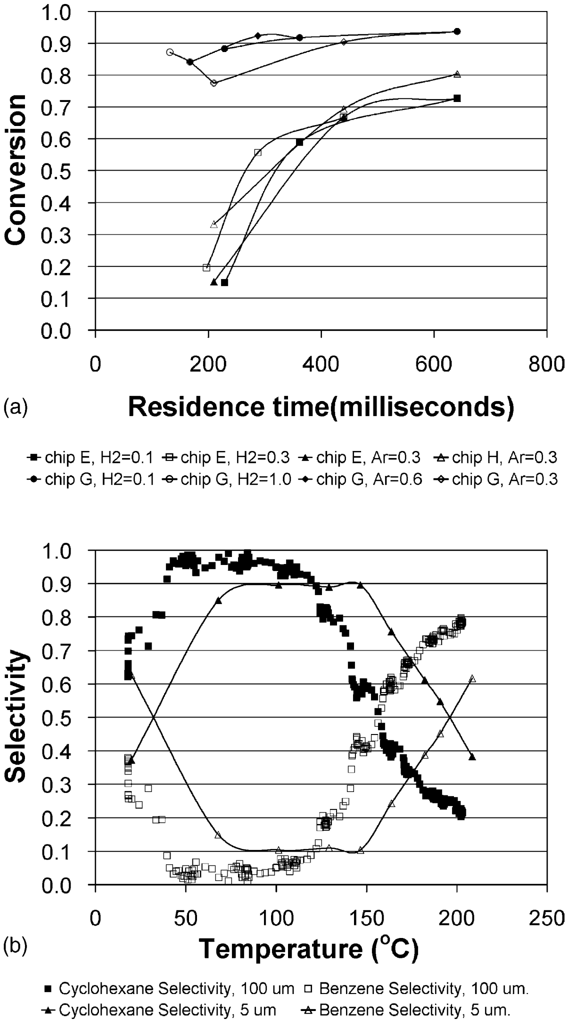

Fig. 3. (a). Conversion vs. residence time: (a) $T = 200$ °C, $P = 1$ atm for chip E (100 μm width), H (100 μm width) and G (5 μm width). (b) Shift in product selectivity at increasing temperatures. Benzene selectivity increases at higher temperatures, as dehydrogenation becomes the favored reaction.

3.2. Methanation

Methanation reaction has been chosen as a preliminary syngas conversion study leading to F–T synthesis, despite the difference between the mechanisms of methanation and F–T synthesis. Both iron and cobalt coated microreactors were used to carry out the reaction, as shown in Eq. (3):

$$CO + 3H_2 \xrightarrow{Fe,Co} CH_4 + H_2O \quad (3)$$

Among the various transition metals (Fe, Co, Ni, Ru, etc.) that have been explored for syngas conversion, Fe and Co based catalysts are most used in industry [6,24,25]. Iron based catalyst is favored mostly because of its low cost, while cobalt based catalyst has the advantages of mild operating condition requirements, no water shift reaction, and slower deactivation rate [24,25].

The initial experiments involved studying catalyst behavior over a period of time and the effect of temperature and H_2/CO flow ratio on conversion. Catalyst activation period ranged from 10 to 15 h under conditions of $H_2 = 0.3$ sccm, $CO = 0.1$ sccm, $T = 200\,^{\circ}C$ and $P = 1$ atm. This observation illustrates the utility of our approach for characterizing activation behavior [25]. Then H_2/CO flow ratio was maintained at 3:1 (0.3 sccm: 0.1 sccm) and temperature was stepped with the result that methane conversion improved with increasing temperature. From the experiments on two iron based and two cobalt based 100 μm-width reactors, we found that iron has a higher catalyst activity than cobalt, which correlates to the literature [25]. For iron-coated reactors, the conversion ranged from 28 to 70%, while only 5 to 18% for cobalt catalyst, at temperatures between 200 and 250 °C (the lowest and highest reaction temperature were 175 and 300 °C, respectively), as shown in Fig. 4. No detectable water-gas shift reaction was detected, nor was catalyst deactivation observed during the experiments for both Fe and Co based reactors, ranging from 9 to 25 h. The conversion of reactor Fe-120801 is thought to be abnormally high especially in comparison to the result of Davis et. al. [26]. This anomalous behavior is felt to be an experimental effect due, for example, to a poor fluidic seal. We include this data as we have yet to ascribe a reason for discounting it.

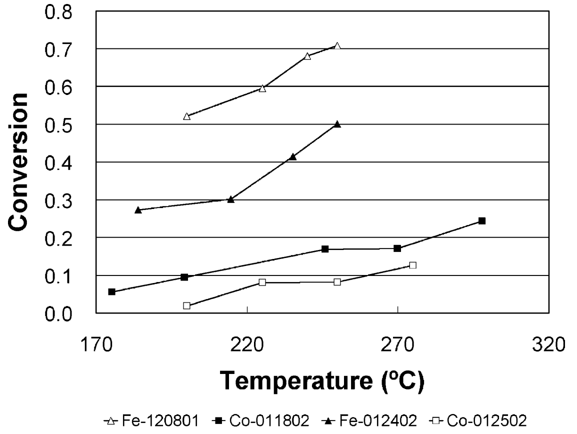

Fig. 4. Methane conversion vs. time at H_2:CO = 3 : 1, with temperature ranging from 175 to 300 °C; 1 atm pressure.

Another experiment was carried out with a Fe coated 100 μm-width reactor (Fe-120801) at 250 °C while H_2/CO flow ratio was varied from 1:1 (H_2 and CO flows both 0.1 sccm) to 10:1 (1.0 sccm: 0.1 sccm) and results are shown in Fig. 5. Although the stoichiometric H_2/CO feed ratio for this reaction is 3:1, we observed an increase in conversion with higher H_2/CO ratio. This observation is in agreement with literature reports concerning the difference in chemisorption ability of H_2 and CO onto the catalyst surface. It is

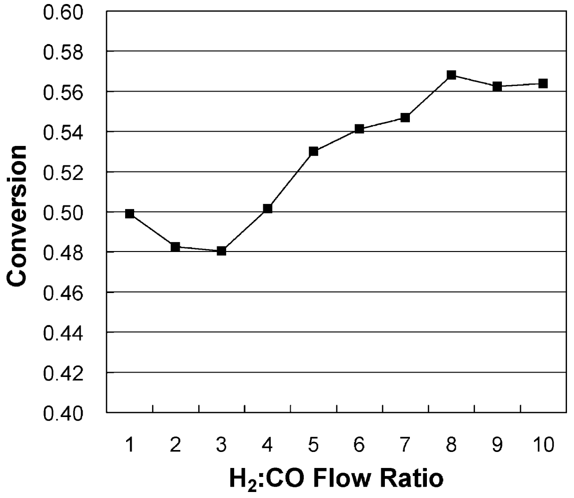

Fig. 5. Conversion vs. H_2:CO flow ratio at 250 °C, $P = 1$ atm with H_2:CO ratio held constant during each 40 min cycle.

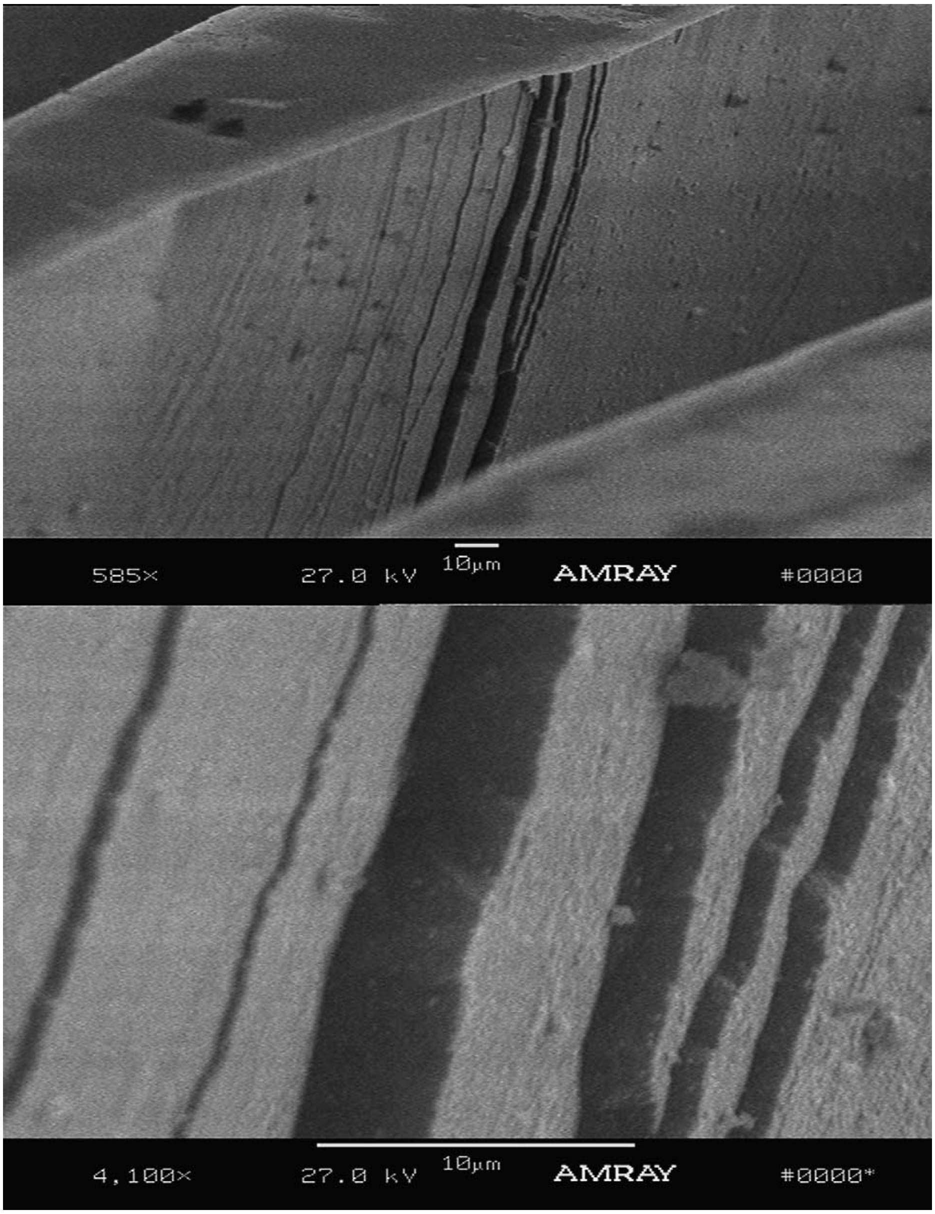

Fig. 6. SEM photos of carbonaceous layer on the wall of microchannel due to Boudouard reaction.

widely believed that it is the low hydrogen adatom concentration that limits the methane formation rate [27–30].

An interesting phenomenon we observed for reactor Fe-120801 is a significant overlayer deposition on the reaction zone of the microreactor after reaction at 250 °C over 72 h, as shown in Fig. 6. Discoloration of the metallic catalyst surface was visible with the naked eye during the course of the experiment. According to scanning electron microscope and X-ray photoelectronic spectroscopy study, we believe a carbonaceous layer was formed according to the Boudouard reaction with disproportionation of CO [25].

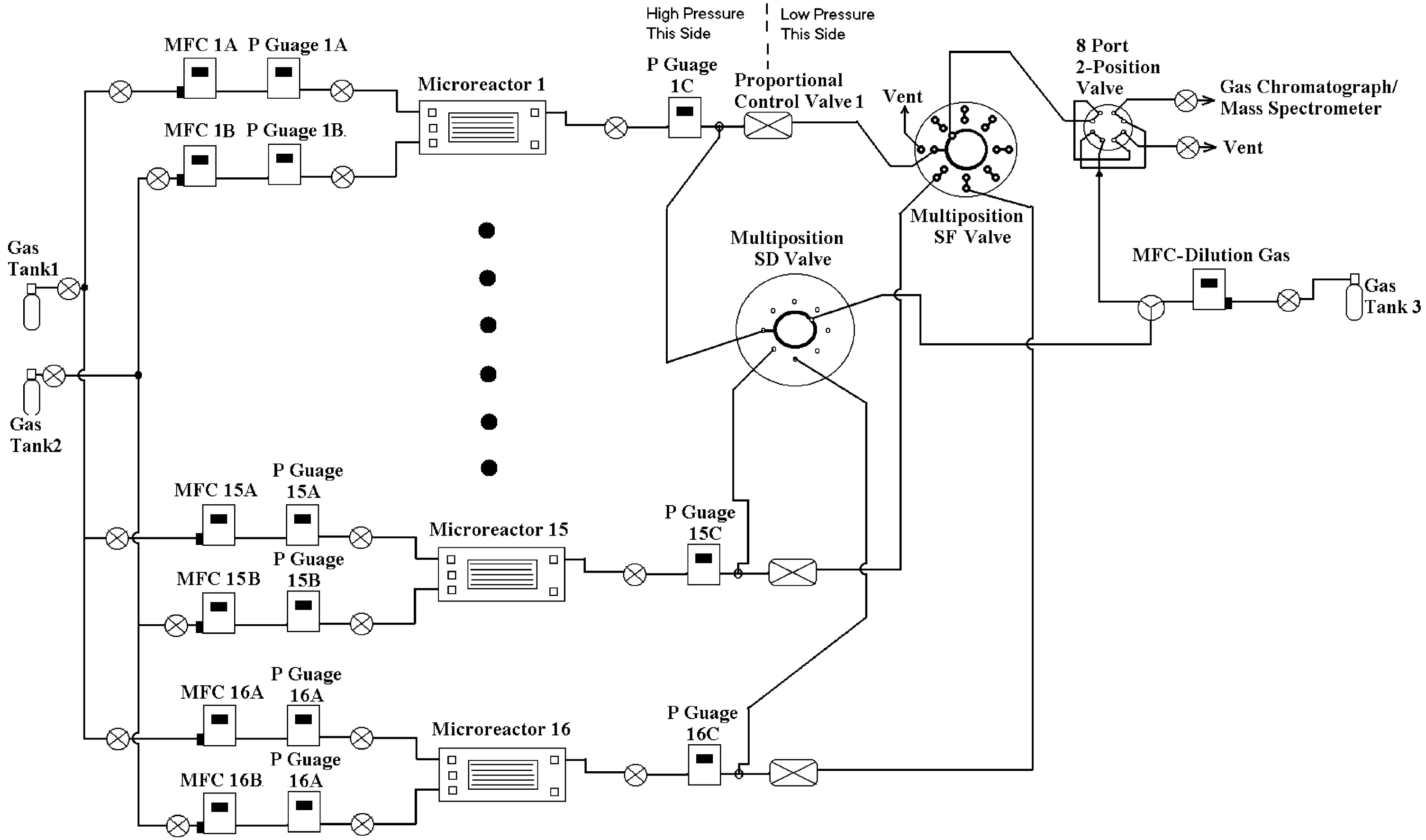

Fig. 7. Schematic of microreactor-based parallel catalyst analysis system.

Table 1
Comparison of our old microreactor system and the new parallel microreactor system

	Single reactor system	Reactor array system
No. of reactor(s)	1	16
CO consumption per hour per reactor	Min: 7.5 mg (6 sccm); max: 75 mg (60 sccm)	Min: 7.5 mg (6 sccm); max: 750 mg (600 sccm)
H_2 consumption per hour per reactor	Min: 0.54 mg (6 sccm); max: 5.4 mg (60 sccm)	Min: 0.54 mg (6 sccm); max: 54 mg (60 sccm)
Maximum operating temperature	<300 °C	>500 °C
Maximum operating pressure	<100 psig	500 psig
Online analysis system	MS	MS & GC
Lab floor space	1 m^2	2 m^2

4. Current work on microreactor array system

Based on our experience on single microreactor system development, a parallel microreactor system is being developed (Fig. 7). This system promises to further hasten the catalyst development process with automatic control and data acquisition. Moreover, precise process control (reactant concentration, temperature and pressure control), flexible experiment operation (adding or reducing reactant lines, variation of catalyst composition) and low operation/maintenance costs are also distinct advantages of this system. Table 1 shows the comparison of our old microreactor system and the new parallel microreactor system.

Commercially available multi-position (16 positions and 2 positions) valves are used to connect this array of microreactors with gas chromatograph/mass spectrometer as shared gas analyzers. Gas flow controllers, pressure gauges/proportioning solenoid valves, resistive heaters/thermocouples are applied in the system for flow, pressure and temperature control, respectively. Controlled by the LabVIEW™ program, multiposition valves can switch from one reactor line to another in milliseconds, such that a dozen catalyst candidates can be scanned and analyzed by the gas analyzer in parallel. Synchronized with flow, temperature and pressure data (also saved by the LabVIEW™ program), complete reaction information is acquired and further analyses pertaining to conversion, selectivity, rate law deduction, etc. can be done expediently.

The system is designed to handle high-temperature (room temperature to 500 °C) and high-pressure (vacuum to 500 psig) reactions, which satisfy the needs for characterizing industrial F–T synthesis conditions [25]. Our devices have been reliably tested at temperatures of 450 °C and pressures of 100 psig, being limited at present only by the ability of peripheral equipments to establish these conditions [31,32]. Moreover, design concepts pertaining to F–T reaction environments, for example, multiphase reaction capability, dealing with solid (wax) accumulation, recycle, etc. will be developed, with the goal of more closely approximating industrial F–T synthesis. Future work is to be done to compare our results to the F–T reactions studied in bench scale and industrial scale processes.

5. Conclusions

The microreactor and characterization setup described here show great promise for a new breed of laboratory reactors requiring less infrastructure and producing quality data with fast turnaround. Because of the size advantage, a parallel catalyst analysis system is made possible for rapid F–T catalyst development, with the goal of a scale-up at the industrial level. Future work concentrates on the exploration of detailed F–T reaction mechanisms, control of catalyst candidate composition and structure, and industrial F–T process approximation in the microscale. Other model reactions will also be studied in an attempt to gain broad experience with the device in a variety of chemical reaction applications.

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