

The Catalytic Partial Oxidation of Methane in a Microchannel Chemical Reactor

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Abstract

Microchannel reactors are a rapidly emerging technology field. The throughput level of conventional reactors is maintained while dramatically reducing the size of a chemical reactor by several orders of magnitude. High processing rates are achieved in microchannel reactors because heat and mass transport limitations are reduced through parallel processing in many small channels. The initial targets for these reactors are fast exothermic reactions, including methane partial oxidation (POx) to synthesis gas, where fast processing rates favor non-equilibrium chemistry and high product selectivity. Methane POx was investigated in this study using a rhodium-based catalyst in a microchannel reactor, and a non-equilibrium product distribution was observed.

Introduction

Microchannel reactors offer the promise for reducing the size of conventional chemical reactors because intrinsic rather than apparent kinetics are realized. Heat and mass transport limitations that reduce the apparent reaction kinetics are minimized in microchannel reactors by reducing the effective transport distance. A much smaller boundary layer is found within each microchannel than that found in the bulk flow of a conventional reactor. As the boundary layer shrinks, the corresponding contribution of slow conduction and diffusion to the heat exchange or catalyst surface is reduced. This overall reduction allows the achievement of intrinsic kinetics in a high throughput reactor. This system can also be considered as one where the effectiveness factor approaches unity.

One application for this technology is distributed hydrogen production. The small modular nature of microchannel reactors enables the placement of hydrogen generation near the point of use for a fuel cell or for other applications. Methane is a feedstock that fits well with the distributed nature of this technology, because the existing natural gas pipeline infrastructure makes it readily available and accessible at any point along the distribution chain. Hydrogen is the desired product from methane and is required by stationary Proton Exchange Membrane (PEM) fuel cells to produce electrical power at central stations, substations, or residences. Currently, hydrogen is industrially produced from methane steam reforming in a conventional fixed-bed technology, that is not well-suited for miniaturization.

Partial oxidation (POx) of methane to synthesis gas is the initial conversion technology investigated in a microchannel reactor. POx processes are fast exothermic reactions, that can benefit from microchannel reactors because the generated heat can be rapidly removed from the system using highly efficient embedded microchannel heat exchangers. Hot spots and the potential for thermal runaway in conventional catalytic systems, makes this application well suited for microchannel reactors.

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Background

The POx reaction produces synthesis gas (CO and H₂) from methane and air. Oxygen is carefully maintained at the synthesis gas ratio while the reaction is run at high reaction temperatures and short contact times. Recent literature (Hickman and Schmidt 1993) explored partial oxidation reactions based on the concept of millisecond residence times and showed that extremely high synthesis gas yields (>90%) can be obtained from methane. Short residence times and high reaction temperatures form synthesis gas on rhodium catalysts while simultaneously inhibiting combustion products and coke. It is reported that the activation energy for hydrogen overoxidation is higher on rhodium than other catalysts, including platinum, which makes this catalyst preferred. Millisecond reaction times are critical to stop the series reaction at the synthesis gas products.



Microchemical systems are well suited for designing and deploying compact reactors with millisecond reaction times because of the rapid thermal quenching that results from integrated microchemical heat exchangers (Call et al. 1996; Srinivasan et al. 1996; Tonkovich et al. 1996). Rapid heat production from the exothermic reaction is quickly removed through a microchannel heat exchanger to quench the desired reaction products. In addition, these processes are run under near isothermal conditions to prevent hot spots, thermal runaway and possible explosions. Thermal excursions are an extremely serious consideration for conventional reactors, where low heat removal rates require high reactant dilution with an inert, or operation that only permits a few percent conversion per-pass.

The microchannel reactor has inherent safety and thus scalability features. The most striking inherent safety feature of a microchannel reactor is the low reactant inventory that eliminates the accumulation of flammable gases which are well within the explosion regime. In addition, microchannels behave much like a flame arrestor placed in conventional systems because the channel dimensions are designed to be equal or smaller than the explosion quench diameter.

A patented microchannel reactor that uses a planar sheet architecture is described in this paper (patent #5,611,214). Component functions, including the mass conversion and heat addition, are achieved by stacking sheets into a compact device. Each sheet contains the appropriate number of parallel (straight or non-straight) microchannels for rapid heat and mass exchange, headers, footers, and manifolding to prevent flow maldistribution.

The optimal microchannel dimensions vary depending upon the reaction. Typically, channels have heights and widths between 100 μm and 1000 μm, and channel lengths of a few centimeters. Channel dimension optimization is a function of heat removal rates, reaction kinetics, and pressure drop requirements. Process scale-up is achieved by adding more parallel channels, or clusters of channels (a cell, or a unit cell).

Experimental

A microchannel reactor was investigated with the partial oxidation of methane to synthesis gas. Existing reactor hardware was modified to determine the feasibility of this approach. Active catalyst powders were housed within the reaction zone to initiate the desired reaction sequence. While the use of catalytic

powders is not feasible for full-scale operation because of pressure drop considerations, it does provide a basis for determining the applicability of microchannel reactors for fast exothermic reactions. Current research efforts are focusing on new reactor designs and the development of engineered catalyst microstructures that are active and provide low pressure drops for high throughputs.

Catalyst Preparation

A rhodium (Rh) catalyst impregnated on a mesoporous silica (PQ SiO₂) support is used in all reported experimental trials. The catalyst was prepared by incipient wetness impregnation of the powdered silica with a rhodium nitrate (Rh(NO₃)₃) solution. The loading for Rh is 5% by weight. A solution of rhodium nitrate (10-wt% assay from Engelhard) of appropriate concentration was prepared, corresponding in quantity to the total pore volume of the SiO₂ powders, or slightly less. The rhodium-impregnated silica powders were dried at 100 °C in vacuum overnight, followed by calcination at 350 °C for at least one hour. The catalyst was reduced with 10% H₂/He at 120 °C for at least one hour prior to the catalytic testing.

Fabrication Methods for Microchannel Reactors

The microchannel reactor consists of nine stacked metal sheets. The base material is stainless steel and each sheet has the appropriate number of channels, headers, footers and flow paths cut from the metal by either conventional machining or electrodischarge machining (EDM). Figure 1 shows the configuration of the reactor sheet (7 cm x 3.8 cm x 0.4 cm). The channels are 254-microns wide, 1500-microns deep and 3.5-cm long. The total width of the cluster of microchannels (a cell) is 1.85 cm. Each fin is 254-microns wide. The reactor section contains 37 parallel channels and 36 fins with a triangular header and footer that facilitates uniform flow through each channel.

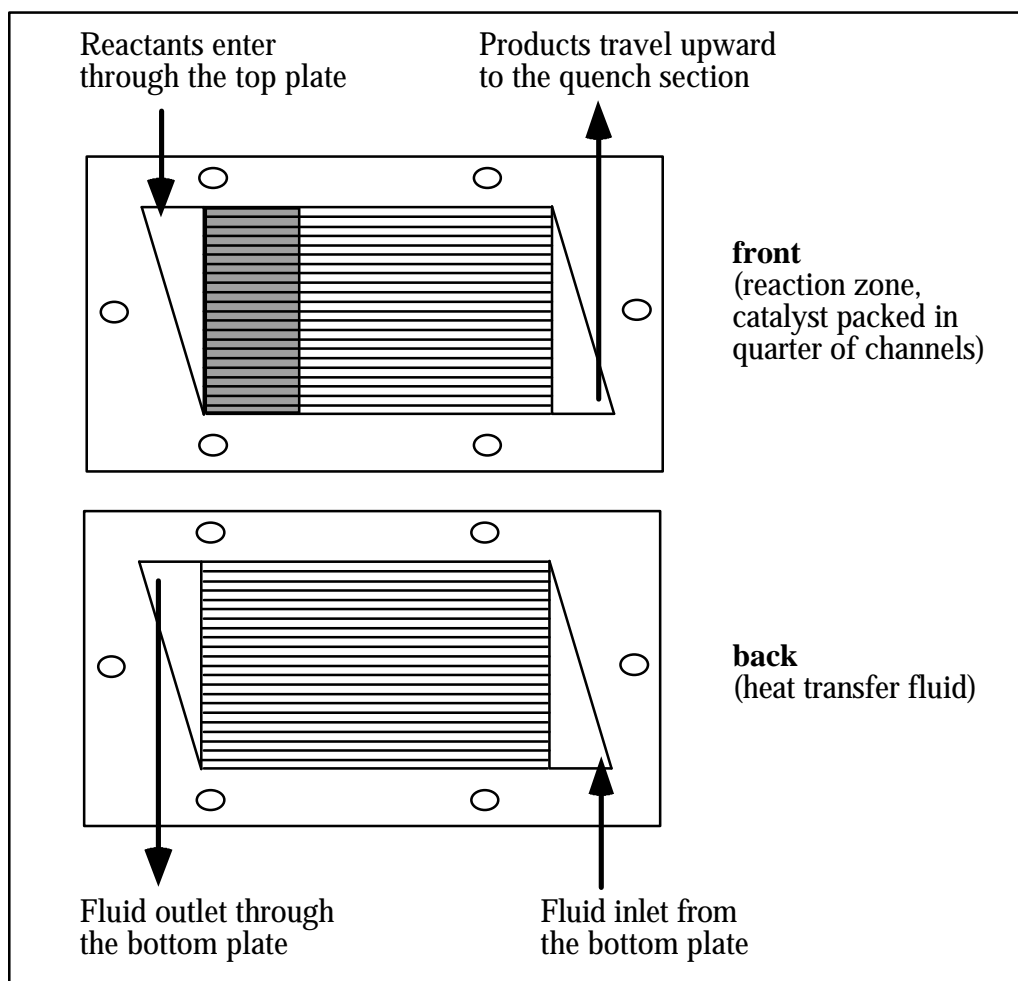


Figure 1. Reaction sheet within the microchannel reactor

Microchannel reactor configuration and operation

A catalytic microchannel reactor system is configured in a multiple sheet planar architecture and is shown in Figure 2. The reactor system includes a reaction zone, a reactant preheat section, a product quench section, and a heat generation section. The catalyst is packed either within the microchannels of the reactor plate or within the microchannel header of the same plate.

The reactor plate is sandwiched between two integrated heat exchangers which provide the heat necessary to obtain light-off for the partial oxidation of methane. The combustor heat exchanger preheats an air stream, which is dedicated as a heat exchanger fluid. This air stream flows countercurrent to the surrounding gas streams. The third heat exchanger allows for the quenching of the product stream.

The reactant feed gases (methane and oxygen) are fed to the preheat heat exchanger plate using MKS Instruments mass flow controllers. The mixed feed gas stream flows countercurrent to the “hot air” stream before entering the POx reactor plate. The product gases are then directed through the quench section and sent to an on-line gas chromatograph, where the product stream is analyzed.

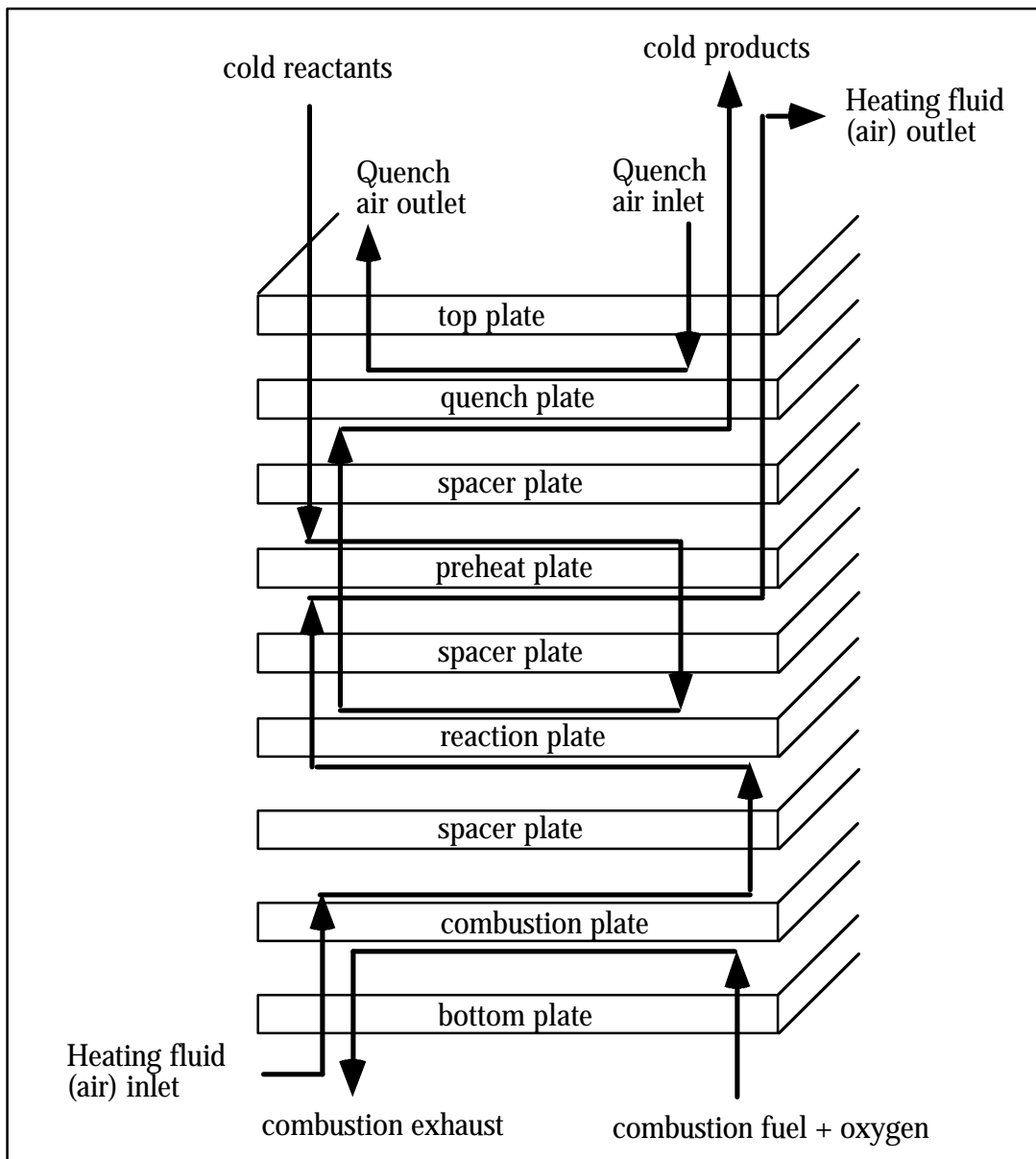


Figure 2. Microchannel reactor configuration

Two thermocouples are strategically placed inside the microchannel catalytic reactor system. One thermocouple is located in the header of the combustor plate for monitoring the sustainability of the combustion flame. The second thermocouple comes in contact with the airside of the quench heat exchanger plate. Direct *in situ* measurement of the temperature within the catalyst bed is not possible with the available thermocouples, because the thermocouple diameter is greater than the width of the microchannels where the catalyst is packed. Subsequent designs are addressing this issue.

An electronic pressure transducer is used to measure the differential pressure across the catalyst bed. This transducer detects pressures on the order of 10 inches of water, adequate for the observed pressures.

Reactor Sealing

Nickel gasket material is used to seal the individual plates of the microchannel reactor system. The metal was obtained as 0.005 inch thick sheets from Goodfellows Corporation. Six stainless steel bolts (10-24), equally spaced along the long sides of the microchannel system, are used to compress the gaskets and hold the reactor and heat exchanger plates in place.

Experimental Procedure

Startup of the microchannel partial oxidation system begins with the ignition of the combustor. Combustion fuel (in this case, methane) and oxygen are turned on to their predetermined stoichiometric flowrates. The flame is ignited by inserting a sparking device into the thermocouple port of the combustor plate, where it comes in contact with the combustible gas mixture. Immediately after the flame is lit, the POx reactor oxygen feed is turned on at a low flowrate. At this point, the oxygen feed serves as a heat exchanger fluid, helping to maintain the microchannel system's overall temperature for safety reasons. It is essential to monitor the temperature of the combustor. A drop in temperature indicates that the flame has been quenched and must be reignited. After the flame has stabilized, the methane flow for the POx reactor is initiated. Reaction conditions are altered by changing flowrates of the combustion gases, the heat exchanger fluids and/or the POx reactants.

Analysis

On-line analysis of the reactants and products was performed with a M200D gas chromatograph from Microsensor Technology, Inc. The gas chromatograph uses two columns to detect all gases of interest. A Molecular Sieve 5A column analyzes for hydrogen, CO, methane, oxygen and nitrogen. Carbon dioxide is detected with a Poraplot U column. The Molecular Sieve 5A column uses argon as its carrier gas and the Poraplot U uses helium. Both carrier gas flowrates are pre-set at 6 cc/min. Oven temperatures are set at 100 C for the Molecular Sieve column and 59 C for the Poraplot U column.

Calculations

The reported selectivity and conversion calculations were based on the measured concentration of gaseous products and shown in equations 1-4.

$$S_{CO} = n_{CO} / (n_{CO} + n_{CO2} + n_{C(s)}) \quad (1)$$

$$S_{H2} = n_{H2} / (2 * \text{moles of } CH_4 \text{ in feed}) / X_{CH4} \quad (2)$$

$$S_{C(s)} = 1 - (n_{CO} + n_{CO2} + n_{CH4}) / \text{total moles of } CH_4 \text{ in feed} \quad (3)$$

$$X_{CH4} = 1 - n_{CH4} / (n_{CH4} + n_{CO} + n_{CO2} + n_{C(s)}) \quad (4)$$

The reported equilibrium conversion and selectivity values as a function of temperature were determined using the FACT™ thermodynamic software.

Results and Discussion

Several preliminary experiments were conducted to determine how suitable microchannel reactors are for fast exothermic reactions. The catalytic partial oxidation of methane was tested with catalyst powders packed within part of the channel region, and then packed in the header region. It is expected that the former will behave in a more isothermal manner, while the latter will mimic an adiabatic reactor. These initial trials were intended to address several questions which serve as a basis for the design of subsequent microchannel reactors that are more well-suited for this reaction. The primary issues are as follows:

- obtaining non-equilibrium chemistry and high hydrogen yields
- determining the contribution of coking on vessel walls, microchannels, and on the catalyst surface
- the ability to reach and sustain the desired operating temperatures
- the ability to remove the exothermic reaction heat
- assessing the overall reactor operating characteristics

The first set of preliminary tests investigated the effect of catalytic powders packed within the microchannels. The top quarter of the channels were packed with 25 mg of the 5 wt% Rh/SiO₂ catalyst. Quartz wool was packed behind the powders to keep them in place. The methane feedrate was 100 sccm and oxygen was fed at the stoichiometric value of 50 sccm. The effective reactor volume was 0.1233 cc, which corresponds to a residence time of 49.3 milliseconds at STP. The measured pressure drop was less than 250 Pa.

After initiating heating through methane combustion in a separate section, the reactor temperature increased as a function of time. Over the course of two hours the reactor temperature rose above 700 C (measured as a gas phase temperature at the quench section inlet). At that temperature, a leak in the reactor plate occurred and the operation was ceased. Between 300 C and 700 C, experimental results were compared to equilibrium values and shown in Figures 3 and 4.

The measured selectivity reveals a non-equilibrium product distribution (Figure 3). Copious quantities of coke are predicted, but do not form with the short contact time microchannel reactor. Further, the formation of combustion products, carbon dioxide and water, are also below equilibrium values. The selectivity of carbon monoxide exceeds the equilibrium prediction, while the hydrogen selectivity does not. This latter result is not surprising, considering that the equilibrium hydrogen selectivity includes a large contribution of hydrogen formation with carbon deposition. It is also expected that our non-optimized configuration and operation may promote unwanted hydrogen oxidation to water. Figure 4 compares the predicted equilibrium methane conversion with that observed in the microchannel reactor.

An important consideration for evaluating these data is the temperature measurement. The temperature of the hot gas stream at the quench plate inlet is the reported reaction temperature. This most likely does not reflect the actual temperature in the reaction zone, nor on the catalyst surface. This initial reactor design is not well suited for direct reactor temperature measurement. Further this design does not closely match heat removal with the reaction zone, which promotes adiabatic reactor operation.

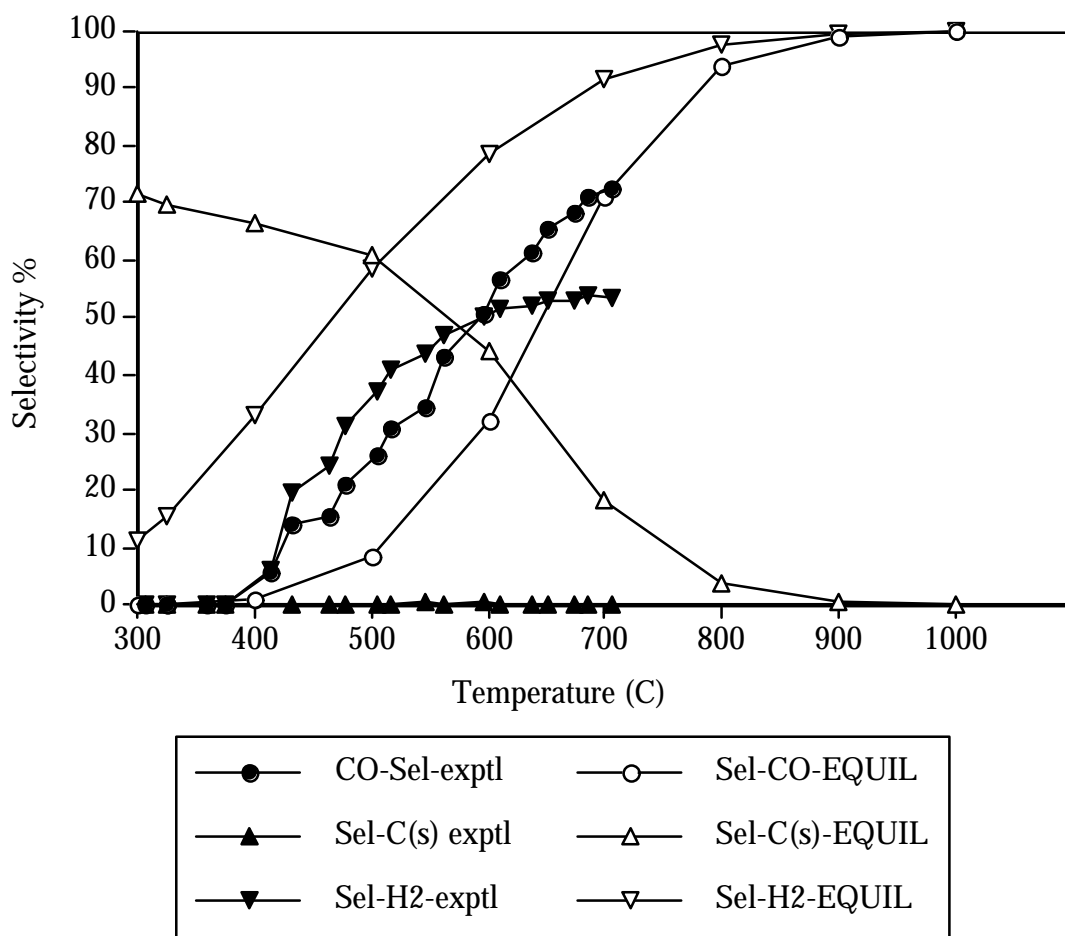


Figure 3. Selectivity for methane partial oxidation: experimental vs. equilibrium

In the second set of preliminary tests, the microchannel header was packed with 20.3 mg of catalyst powders. The header volume is 0.105 cc. Identical feedrates were used in this set of experiments as those reported previously. The total inlet feedrate is 150 sccm, which corresponds to a residence time of 42 milliseconds at STP. The reactor initiation followed a similar but faster procedure (reactor heat up in less than an hour), but a leak was detected at a slightly lower temperature (below 600 C). Figure 5 shows the selectivity results and compares these results to the equilibrium values. The measured methane conversion was near 50% for each trial, indicating that the actual temperatures within the reaction zone may have been much hotter than our distant measurements indicate. The results also indicate that the time at each temperature may not have been sufficient for thermal equilibration. Again, very little if any coking is observed (measured from the total carbon balance). The experimental values of carbon monoxide and hydrogen selectivity exceed the equilibrium values, but the hydrogen selectivity is below the expected stoichiometric value from synthesis gas production. Oxidation of hydrogen is the expected cause in this non-optimized reactor.

In both sets of these early trials, a few issues were identified and others were resolved. The need for a more robust reactor design (and sealing protocol) is required to obtain the desired operating temperatures of 900 C and higher for this reaction. The location and composition of the catalyst is also critical. A robust catalyst with engineered microstructures, rather than powders, is required for scale-up to achieve

high production throughputs. The integration of rapid heat removal is also needed in new reactor designs to prevent hot spots and thermal runaway as the heat formation rate increases with throughput. Each of these issues is currently being addressed in the next generation of microchannel reactors.

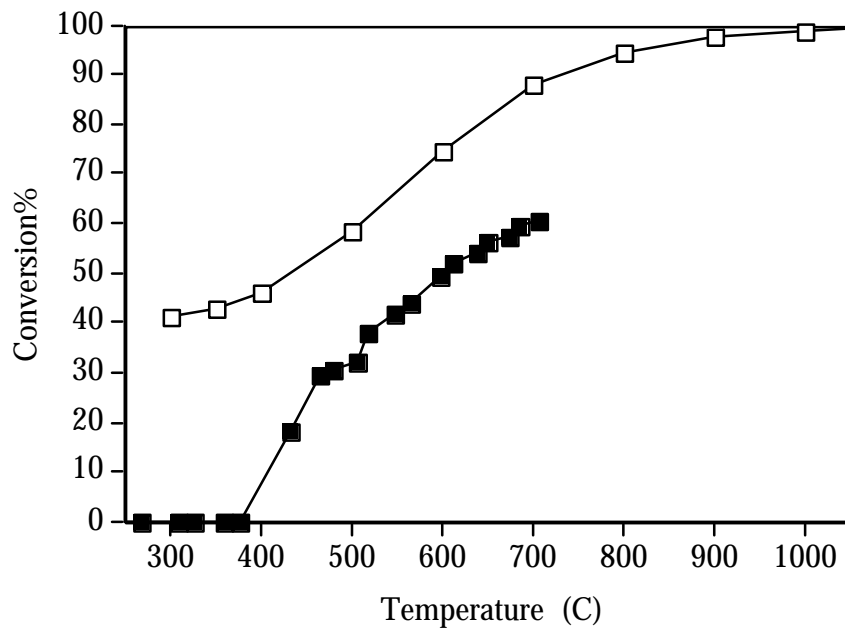


Figure 4. Methane conversion: experimental vs. equilibrium

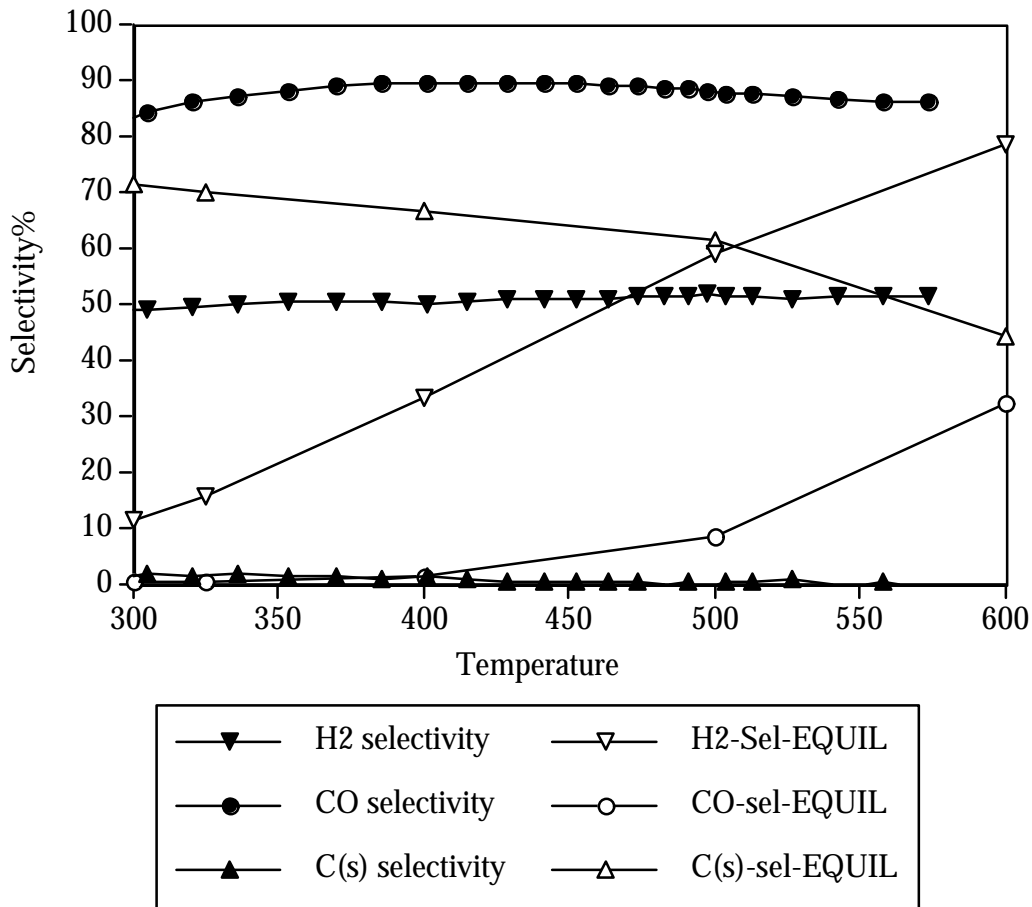


Figure 5. Selectivity for methane POx with catalyst packed in the header

Conclusions

A microchannel reactor was used to demonstrate non-equilibrium chemistry for methane partial oxidation. This short contact time reaction is well suited for the microchannel reactor architecture. Ultimately, this novel reactor concept will be instrumental for the deployment of small compact processing units that produce hydrogen on demand for fuel cell applications.

Acknowledgments

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