Hydrogen Production in a Reverse-Flow Autothermal Catalytic Microreactor: From Evidence of Performance Enhancement to Innovative Reactor Design

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There has been significant recent interest in the development of low-temperature fuel cells for portable power generation because of their potentially very high efficiency and ultrahigh density of power generation. In many cases, hydrogen is a preferred fuel for use in fuel cells because of its very high energy density. In this paper, we report the first experimental evidence that autothermal reverse-flow operation of a microreactor results in up to a 5% increase in reaction selectivity toward hydrogen, a 200 °C decrease in the oxidation ignition temperature, and a reactor “skin” temperature below 60 °C for many hours of stable autothermal operation. Finally, the critical issues in the design of portable catalytic microreactors for small-scale power generation are discussed, leading to the proposed novel, highly integrated planar reactor design aimed at optimal functionality, manufacturability, and low cost.

Introduction

Fueled by the advances in wireless communication technologies and the Internet, a competitive portable electronic device must have increased intelligence (computation power), feature broad connectivity (bandwidth), and be always on. These requirements create an ever-increasing demand for the development of small-scale, highly efficient, “palm” power sources.1 Unfortunately, improvements in power technology have not kept up with Moore’s law for the rate of increase in computation power and bandwidth.2 The existing battery technologies become a major obstacle to future advances in portable communication devices, and fuel-cell-based energy sources appear to be the only viable candidate for battery replacement because of their potentially very high efficiency and ultrahigh density of power generation. Two main types of fuel cells are currently being actively developed for portable applications. These are hydrogen-based fuel cells with external fuel reforming (i.e., conversion to hydrogen) and direct-methanol fuel cells, in which methanol (the fuel) is directly oxidized at the anode.1,2 In many cases, hydrogen is a preferred fuel for use in fuel cells because of its very high surface power density.1

Among various alternatives, the production of hydrogen-rich synthesis gas (H2/CO mixture with some CO2, H2O, and N2) followed by separation of the hydrogen from the steam is one of the most economically viable processes for hydrogen generation from commonly available hydrocarbon fuels. In the case of methane, for example, the catalytic conversion process is based on either catalytic partial oxidation (CH4 + 0.5O2 → CO + 2H2, ΔH_298 = −35.7 kJ/mol) or steam reforming (CH4 + H2O ↔ CO + 3H2, ΔH_298 = 206.2 kJ/mol). Each approach has its fundamental advantages and limitations: partial oxidation is exothermic (i.e., heat is released as a result of reaction) and offers compactness, fast startup, and rapid responses to feed changes; steam reforming is endothermic (i.e., requires external heating) but produces higher concentrations of hydrogen and results in higher system efficiencies.3 In addition, the highly exothermic, homogeneous and heterogeneous/catalytic total oxidation or combustion reaction (CH4 + 2O2 → CO2 + 2H2O, ΔH_298 = −802.3 kJ/mol) could also occur, which does not produce hydrogen but provides a significant source of energy. Neither of these reactions can be run in isolation, and the dominance of any specific reaction pathway is determined by the feed mixture composition, temperature, and catalyst. Thus, there is an opportunity to combine a strongly exothermic partial oxidation with endothermic heterogeneous steam reforming to achieve much higher efficiency for the hybrid process. Further, because the overall process is slightly exothermic, it can be effectively executed in a reverse-flow catalytic reactor.4,5 Figures 1 and 2 depict the expected temperature and species concentration profiles during reverse-flow operation of such a reactor. In this transient regime, the reactor is first preheated to a uniform temperature to ignite the partial oxidation reaction, and then, it continuously operates via autothermal heat regeneration accomplished by periodic flow reversal. In other words, as the upstream part of the reactor is progressively cooled by the cold reactants, fuel partial oxidation takes off, and the temperature wave propagates through the reactor in the direction of the flow (Figure 1a). The flow is reversed before the reaction zone reaches the exit of the reactor, and this causes the high-temperature wave front to move in the opposite direction (Figure 1b). After several flow reversals, a quasi-steady-state temperature profile is established in the reactor with an extended zone of approximately uniform elevated temperature in the middle of the reactor (optimal conditions for the endothermic steam reforming reaction) and decreasing temperature profiles.
on both ends of the reactor (optimal conditions for the exothermic oxidation and water-gas shift reactions), thus resulting in maximum reaction conversion and selectivity. Thereby, the heat is effectively retained inside the catalytic reactor, and no additional external reheating is needed. In addition to favorable autothermal operation, the oscillatory motion of the high-temperature wave in the reactor leads to gasification and removal of the carbon/soot, which is potentially deposited on the catalyst as a result of the endothermic methane cracking and exothermic Boudouard reactions. The reverse-flow operation of the reactor makes it possible to generate and control spatiotemporal patterns of temperature, concentrations, and catalyst states that cannot be attained under steady-state operation. Such operation also offers opportunities for exploiting catalyst dynamic properties and optimal placement (Figure 2), and it results in lower average operating temperatures, thereby reducing the pressure drop and heat losses.

The chemical processing rates in heterogeneous microreactors increase significantly as a result of a decrease in resistance to species transport caused by a drastic reduction in the thickness of the boundary layer. Ideally, with a decrease in the channel size (diameter), one hopes to achieve operation at the intrinsic rate of the reaction and to maintain a sufficiently large reactor throughput by using the parallel chemical processing in many small channels comprising the reactor. In addition to rapid heat and mass transport, the miniaturization of chemical reactors results in high productivity rates through fast nonequilibrium surface chemistry, as well as opportunities for energy and chemical conversion at the optimal locations. Size limitations pertinent to portable electronics applications and attractive opportunities for process intensification associated with microscale techniques stimulated several attempts to design, fabricate, and test micromachined chemical reactors for hydrogen generation for portable fuel cells. The most notable examples are the early efforts at Pacific Northwest National Laboratory (PNNL), which focused on the development of partial oxidation microreactors, and more recent efforts by Motorola Energy Technology Labs on developing steam reforming microreactors.

Experimental Section

Despite apparent advantages offered by autothermal unidirectional and reverse-flow operation, the experimental data for autothermal reactors are scarce and incomplete. Furthermore, all available data are only for conventional size and not microscale reactors. The most notable works are those of Schmidt and co-workers on autothermal unidirectional partial oxidation of methane in monolith (see ref 8 and references therein) and Ma and Trimm on the use of alternating catalyst beds for autothermal combined oxidation and steam reforming of methane. Only one study, that of Blanks et al., reports the successful experimental demonstration of a large-scale, reverse-flow packed-bed reactor for synthesis gas production. For microreactors, no experimental data have been reported for autothermal reverse-flow operation.

To this end, we report the first experimental evidence that autothermal reverse-flow operation of a microreactor results in increased reaction selectivity toward hydrogen while maintaining the reactor “skin” temperature below 60 °C. The tubular microreactor used in this study (Figure 3a) features a high-temperature ceramic tube (Omega FRX-0201-6) with four holes (500-μm i.d.) as the supporting structure to accommodate high temperatures (up to 1200 °C) specific to catalytic oxidation reactions. A Pt/13% Rh wire (Omega part no. P13R-
We performed detailed experimental studies of the partial oxidation and steam reforming of methane in a tubular microreactor and developed a comprehensive database for reactor performance (reaction conversion and selectivity toward hydrogen) for a wide range of operating temperatures, total flow rate of reagents [expressed in terms of gas hourly space velocity (GHSV) or inverse of the residence time], and feed composition (CH4/O2/H2O) at atmospheric pressure. With this knowledge, we were able to identify the optimal operating conditions for the autothermal unidirectional and reverse-flow operations of the microreactor (summarized in Table 2 corresponding to the test conditions given in Table 1). In Tables 1 and 2, GHSV refers to gas hourly space velocity or inverse of the residence time (in h⁻¹); Tign and Tfinal refer to the ignition temperature of the oxidation reaction and the final skin temperature of the reactor stainless-steel housing (in °C), respectively; and MF refers to the mole fractions of species in the product stream (computed from the partial pressures measured by mass spectrometer). The ignition temperature is defined as the temperature at which a significant spike in the hydrogen generation and methane consumption profiles occurs as detected by the mass spectrometer. Typically, after ignition occurs, the hydrogen and methane concentrations in the product stream change very little with any change in the operating temperature. Reaction conversion is computed as

$$\text{reaction conversion} = \frac{1 - \frac{\text{MF(CH}_4\text{)}}{\text{MF(CH}_4\text{)} + \text{MF(CO}_2\text{)} + \text{MF(CO)}}}{\text{MF(H}_2\text{)}}$$

and the reaction yield is the product of conversion and selectivity. The choice for the above expression for selectivity is stipulated by the fact that endothermic steam reforming is a very slow reaction, so that, in autothermal microreactors operating at relatively high flow rates (small residence times), it is the competition between the very fast partial and total oxidation reactions, rather than between the total oxidation and steam reforming reactions, that dominates the overall system performance. Thus, the selectivity describes an increase in the hydrogen production via partial oxidation and a corresponding decrease in steam production by total oxidation, even when the reaction conversion remains the same.
Our experiments indicate that the optimal methane-to-oxygen ratio in the feed is between 0.7 and 0.9, which results in selectivities in the range of 70–80% and conversions of 55–60% for the unidirectional autothermal conversion of methane to hydrogen, with very little CO content in the product stream. We also found that no steam injection is required for autothermal operation, as endothermic steam reforming is slow and the optimal temperature in the middle of the reactor, which establishes an extended zone of nearly constant temperature in the middle of the reactor, which is optimal for the steam reforming reaction (see Figure 4). The increase in selectivity observed for the reverse-flow operation is due to better thermal management, which leads to a lowering of the peak temperature of the partial oxidation reaction and also the establishment of an extended zone of nearly constant temperature in the middle of the reactor, which is optimal for the steam reforming reaction (see Figure 1a and b). The data points for reverse-flow operation given in Table 1 are the averages of several independent measurements made to ensure reproducibility of the results. These data points were also intentionally selected to correspond to the optimal operating conditions for the autothermal unidirectional reactor [i.e., the optimal feed composition and the total flow rate/GHSV] resulting in the highest conversion and selectivity. Thus, this allows for a comparison of the reverse-flow operation of the microreactor with the best possible case of unidirectional autothermal operation to show that, even for this optimized case, the improvement is quite substantial.

Figure 4 shows a typical MS spectrum, which indicates how the hydrogen yield increases immediately upon imposing flow reversal on the autothermally...
operating microreactor. Flow reversal also allowed for a
decrease in the reaction ignition temperature by as
much as 200 °C, which is essential for the efficient
startup of the cold microreactor. The ignition tem-
perature is dictated by the catalyst used as well as by its
instantaneous redox state. We speculate that the tem-
perature and concentration cycling associated with the
flow reversal establish a favorable redox state of the
catalyst, leading to early “light-off” at lower tempera-
tures. This statement, however, requires further de-
tailed investigation. Another very important result of
this study with respect to application for portable power
generation is that both unidirectional and reverse-flow
microreactors featured very low (below 60 °C) reactor
skin temperatures, as long as they operated in an
autothermal mode. This result owes to minimization of
the distance/time that the heat produced by the exo-
thermic oxidation reaction must travel before it is
consumed by the endothermic steam reforming reaction,
as both reactions essentially occur on the same catalyst
grain. These experiments provide the first experimental
evidence of the advantages offered by the reverse-flow
autothermal conversion of methane into hydrogen in
catalytic microreactors.

Reverse-Flow MicroReactor Design for
Improved Functionality

The simple tubular reactor described above was
simple to build and was used extensively to collect
critical reaction data on the feasibility and performance
enhancement of the autothermal reverse-flow mode of
operation. However, its practical applicability beyond
the laboratory as a portable hydrogen generator is
limited because of the reasons briefly discussed next. A
generic reverse-flow microreactor must include (1) a
mixing chamber where chemical reagents (methane,
oxygen/air, and water) are mixed prior to introduction
to the reaction chamber/section; (2) flow-reversal valve-
s; (3) a reaction chamber/section where the reaction-
(s) ist(are) executed; and finally, (4) pipes and manifolds
to connect system components 1–3 together to establish
a complete, operational system. Among the most desir-
able design characteristics of the complete system are
the following: (i) The dead volume of the flow-reversal
valve should be as small as possible (ideally zero) to
minimize the cross-talk between the unreacted reagents
and reaction products immediately after flow reversal
and, thus, to eliminate the need for purging of the
reactor. (ii) The valve design must be amenable to
simple actuation to ensure overall system robustness
and energy efficiency. (iii) The connecting pipes and
manifolds should be reduced to a minimum or, ideally,
eliminated all together. (iv) It should be possible to place
the mixing and reaction chambers in optimal locations
to achieve additional functionality (for example, to use
waste heat generated in the reaction chamber of the
exothermic catalytic reactor to preheat the reagents in
the mixing chamber, thereby increasing mixing and
energy efficiency).

When dealing with chemical microsystems, in addi-
tion to specific functional requirements imposed on the
reactor design/configuration by the process of interest
(as described above), MEMS (microelectromechanical
systems) (2-D or 2 1/2-D) fabrication technologies impose
further requirements on the design and component
integration of reverse-flow microreactors: specifically,
the layout of individual components must be planar, and
the components must be integrated in a stackable
(layer-by-layer) fashion for low-cost fabrication and
system scale-up.

To address both the functional and manufacturing
challenges, we developed a new design of planar reverse-
flow microreactor that permits efficient (i.e., without any
pipes or connecting manifolds) integration of a mixing
chamber, a zero-dead-volume rotating valve, and a
reaction chamber within a simple and easy-to-manu-
facture reverse-flow system that could be made, in
principle, as small as a dime. The schematic of the
design and operating principles of the proposed system
are shown in Figure 5, and Figure 6 shows photographs
of the prototype reverse-flow reactor, built of stainless
steel on a “large” scale for demonstration purposes. By
configuration13) and loaded with any type of catalyst as complex as one wishes (e.g., a spiral or a Swiss roll reactor (Figures 5 and 6), these chambers can be made for the mixing and reaction chambers of the prototype note that, although single circular channels were chosen reaction chamber in a radial outward direction. Also mixing chamber to capture the heat escaping the within proposed design ideology by placing the reaction into the mixing chamber, and this is accomplished reaction to preheat the feed gases as they are introduced generated as a result of the exothermic partial oxidation should be noted that it is desirable to utilize the heat an established protocol for the dynamic process. It automatic switching of the flow direction according to controller can be readily integrated with the system for mounted on top of the mixing plate with a voice-coil plate. Currently, the switching of the flow direction is done manually; however, a low-power rotary motor mounted on top of the mixing plate with a voice-coil controller can be readily integrated with the system for automatic switching of the flow direction according to an established protocol for the dynamic process. It should be noted that it is desirable to utilize the heat generated as a result of the exothermic partial oxidation reaction to preheat the feed gases as they are introduced into the mixing chamber, and this is accomplished within proposed design ideology by placing the reaction chamber in the immediate vicinity of, but inside, the mixing chamber to capture the heat escaping the reaction chamber in a radial outward direction. Also note that, although single circular channels were chosen for the mixing and reaction chambers of the prototype reactor (Figures 5 and 6), these chambers can be made as complex as one wishes (e.g., a spiral or a Swiss roll configuration13) and loaded with any type of catalyst depending on the specific design requirements of a given application. The small leakage of reagents from the system across the contact plane provides a lubrication layer for smooth relative motion of the top and bottom plates. The loss can be minimized by carefully polishing the contact surfaces or by using intermediate “buffer” cover plates permanently affixed to the mixing and reaction chambers to seal these chambers and leave open only two channels for flow direction switching at the top (see Figure 5). Further, provisions can be made in the design to collect and recycle leaked reagents back into the reaction chamber. Our preliminary experiments indicate the viability of the proposed design concept, and the detailed results will be reported shortly as we complete testing. It is expected that the reactor used in the experiments is outfitted with the same Pt/13% Rh wire (0.005-in. o.d.) as the catalyst, which is wound into a spiral to increase the active surface area for the reaction.

Conclusions

This paper reports the first preliminary experimental evidence that autothermal reverse-flow operation of a catalytic microreactor results in a significant performance gain as compared to unidirectional operation. Specifically, an increase of 5% in the reaction selectivity toward hydrogen was observed, along with an almost 200 °C decrease in the oxidation ignition temperature and a reactor skin temperature of below 60 °C for many hours of stable autothermal operation. The improvement in performance is attributed to an improved thermal management of the reactor and also to a favorable redox state of the catalyst resulting from the temperature and concentration cycling. The achievement of such a low reactor skin temperature is significant from a technological standpoint; however, the question remains whether such a low skin temperature can be achieved with more desirable conversions, and this issue should be investigated using better optimized reactor configurations. The reported results are only preliminary and for a simple unsupported Pt/Rh bulk catalyst, and it is expected that this initial success will stimulate further research in the field of reverse-flow catalytic microreactors. Finally, the critical issues in the design of portable catalytic microreactors for small-scale power generation are discussed, leading to the proposed novel, highly integrated planar reactor design aimed at optimal functionality, manufacturability, and low cost.

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Literature Cited


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