

Microchannel development for autothermal reforming of hydrocarbon fuels

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Abstract

Fuel-processing is a bridging technology to assist the commercialization of fuel cell systems in the absence of a hydrogen infrastructure. The Argonne National Laboratory has been developing fuel-processing technologies for fuel cells, and has reported the development of novel catalysts that are active and selective for hydrocarbon-reforming reactions. It has been realized, however, that with pellets or conventional honeycomb catalysts, the reforming process is mass-transport limited. This study addresses the development of catalysts structures with microchannels that are able to reduce the diffusion resistance and, thereby, achieve the same production rate within a smaller reactor bed. The microchannel reforming catalysts are prepared and tested with natural gas and gasoline-type fuels in a microreactor (diameter: 1 cm) at space velocities of up to $250\,000\text{ h}^{-1}$. The catalysts have also been used in engineering-scale reactors (10 kWe; diameter: 7 cm) with similar product qualities. Compared with pellet catalysts, the microchannel catalysts offer a nearly five-fold reduction in catalyst weight and volume.

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1. Introduction

Proton-exchange membrane fuel cells (PEMFCs) are being developed for electric-power generation in a variety of transportation, stationary, military and portable applications. The PEMFC produces electricity by electrochemically oxidizing hydrogen. In the absence of a hydrogen-refueling infrastructure, however, the successful commercialization of PEMFC system will depend on the ability to convert currently available fuels into hydrogen of acceptable purity.

Production of hydrogen is a well-established process in the chemical industry. The three major approaches for the conversion of hydrocarbon fuels to hydrogen are steam reforming, partial oxidation, and autothermal reforming. The last mention is a chemical combination of steam reforming and partial oxidation. Argonne National Laboratory has articulated the advantages of the autothermal reforming (ATR) process for many applications that face constraints on size, weight, duty cycle, etc., such as in automotive power plants

[1]. In the ATR process, fuel is co-fed with steam and air, and the feed composition is adjusted to maintain a slightly exothermic reaction.

The thermodynamic equilibrium gas compositions form the autothermal reforming of iso-octane and shown in Fig. 1. There are hydrogen concentration peaks at $700\text{ }^\circ\text{C}$, which thus represents the preferred operating temperature [2]. To enable the fuel-reforming process to occur at about $700\text{ }^\circ\text{C}$, a novel, highly active, ATR catalyst system has been developed [3,4]. The system is effective for the conversion of various carbonaceous fuels and has shown excellent resistance to sulfur and coking. Indeed, the intrinsic rates for conversion of hydrocarbons to hydrogen are sufficiently fast for the overall rate of pellet catalysts to be limited by mass-transport limitations.

Given that the mass-transfer resistance can be reduced by decreasing the diffusion path length of the reactants and products to and from the catalyst surface, the microchannel concept was introduced. A new fabrication process has been developed for these structured microchannel catalysts. This potentially inexpensive process has been developed for these structured microchannel catalysts. This potentially inexpensive process provides great control over the geometric dimensions.

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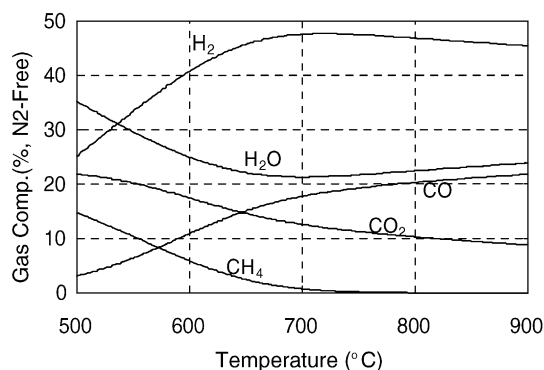


Fig. 1. Equilibrium product gas composition vs. temperature, calculated for reaction between iso-octane (C_8H_{18}), air ($O_2/C_8 = 3.71$), and water ($H_2O/C_8 = 9.11$).

2. Experimental

2.1. Fabrication

The structured microchannel ATR catalyst was fabricated by means of a modified ceramic tape-casting process. Gd-doped CeO_2 with 0.5 wt.% Pt (CGO-Pt) was used the catalyst material, since it had demonstrated excellent activity for the desired reforming reaction. Catalyst powders with specific surface-areas of 5 to $50\text{ m}^2\text{ g}^{-1}$ were dispersed by using commercial dispersion agents and solvents, xylenes and alcohols. The dispersed catalyst slurry was mixed with organic binder resins such as polyvinylbutyral or acryloid. The final slurry was cast at the desirable thickness (50 – $200\text{ }\mu\text{m}$) with a doctor blade and subsequently dried in air. Fugitive materials such as organic fabric can be inserted and the tape retains the slurry phase to leave holes, or thin fugitive materials (1 – $50\text{ }\mu\text{m}$) can be added on top of fully-dried catalyst tape to leave space after the burning

process. The dried catalyst tape maintained flexibility due to the plasticity of the organic binder system and enabled further mechanical treatment such as cutting and rolling. The tape was cut into strips of about 1 cm width and rolled into a ‘jellyroll’ shape of the desired diameter. A small-size microchannel catalysts of about 1 cm diameter prepared for microreactor tests is shown in Fig. 2. The microchannel was loaded inside a stainless-steel microreactor tube and heat-treated to burn the fugitive layer away and sinter the catalyst powder as a self-supported form. After burning of the fugitive layer, well-defined channels were created.

2.2. Characterization of microchannel catalyst

After loading a microchannel in the green state into the microreactor tube, a special heat-treatment was applied to burn out the polymer components and then sinter the microchannel into a self-supporting structure. The polymers were burned out at a slow ramp rate, followed by sintering at a higher ($>500\text{ }^\circ\text{C}$) temperature.

The activity of the microchannel catalyst was studied in the microreactor under varying operating conditions (gas hourly space velocities, GHSV; temperatures) and design conditions (geometries of microchannels such as space thickness, web thickness, and length). Iso-octane (C_8H_{18}), water, and air were used as reactants. Iso-octane and water were provided by HPLC pumps and then vaporized at about $150\text{ }^\circ\text{C}$. The air rate was controlled with a mass-flow controller. The GHSV was calculated with respect to the volume of reactants in the gas phase at $25\text{ }^\circ\text{C}$. The reactor temperature was controlled between 600 and $900\text{ }^\circ\text{C}$, by placing it within a furnace. Temperatures were measured at the top and bottom of the microchannel catalyst by using thermocouples. The product gases were analyzed, by means of a gas chromatograph that was attached to a mass

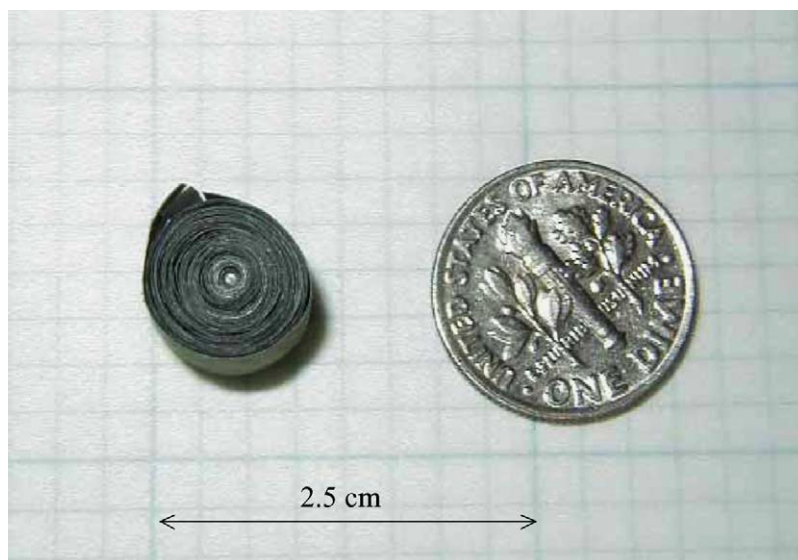


Fig. 2. Microchannel catalyst used for ATR tests in microreactors (1-cm diameter).

spectrometer (HP 6890/HP 5973), after de-humidification of the gases.

3. Results and discussion

The concentration (on a nitrogen- and water-free basis) of hydrogen and by-product hydrocarbons in the product stream from the microreactor, as a function of the space velocity, are shown in Fig. 3. It should be noted that the H₂ after WGS refers to the concentration of hydrogen that would result if the carbon monoxide evolved during the reforming reaction were to be converted to additional hydrogen via the water gas shift reaction (CO + H₂O = CO₂ + H₂). For these experiments, the furnace was set at 650 °C and the feed proportions were adjusted to maintain O₂:C₈ = 3.7 and H₂O:C₈ = 9.1.

Thermodynamic equilibrium calculations suggest that at 650 °C, the product gas should contain 68.7% hydrogen on a dry, nitrogen-free basis. As the plot shows, the microchannel is able to maintain high yields, which compare favorably to the equilibrium level, at space velocities (GHSV) approaching ~250 000 h⁻¹. The concentration of hydrocarbons (such as CH₂) in the product gas shows an inverse correlation with the hydrogen curve. This is to be expected since each mol of by-product hydrocarbon significantly reduces the hydrogen yield, i.e., each mol of methane can be reformed to yield 4 mol of hydrogen.

The hydrogen yields (before WGS) achieved with pellet catalysts and the microchannel catalysts are compared in Fig. 4. It is evident that the microchannel catalyst outperforms the pellet catalyst. This supports the hypothesis that the microchannel-structured catalyst reduces mass-transport limitations. The advantage of the microchannel structure is especially true at higher processing rates.

In order to address the effect of the channel design on the pressure drop, two types of microchannel were fabricated and studied. Scanning electron micrographs of two different types of microchannel are presented in Fig. 5, namely,

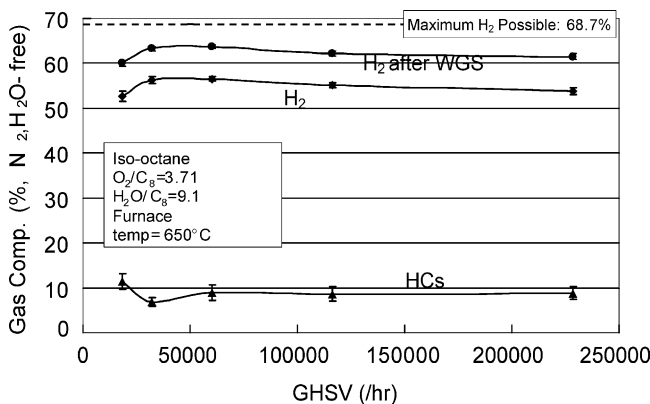


Fig. 3. Conversion characteristics of microchannel catalyst of iso-octane ATR reaction.

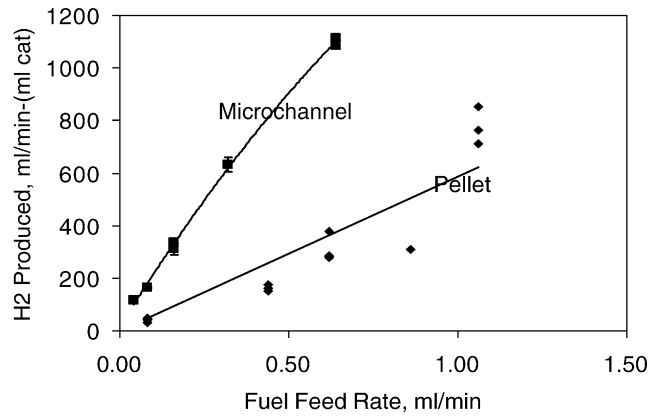


Fig. 4. Comparison of ATR microchannel and pellet-type ATR catalysts for iso-octane as function of rate of fuel feed.

a ‘closed’ microchannel and an ‘open’ microchannel. The diameter of the void (noted as ‘d’) in Fig. 5(a) and the void thickness (noted as ‘s’) in Fig. 5(b) can be easily controlled by using fugitive materials of different diameter or thickness; a void thickness of the order of 1 μm is easily achieved. Such dimensions are not possible in commercially available, honeycomb-type, cordierite supports. The open-type microchannel exhibits a very low pressure drop in this study. A simple model (Fig. 6) has been established to estimate the pressure drop, i.e.,

$$\frac{\Delta P}{L} = \frac{8\mu c M N_s}{\pi \rho n_s (n_s + 1) s^3} \quad (1)$$

$$\Delta P = \frac{8\mu c(L)}{\pi \rho (d)} M \frac{4(w + s)}{(2w + 2s + d) s^3} \quad (2)$$

$$N_s \equiv \frac{\text{no. of spiral turns}}{\text{unit length}} = \frac{1}{s + w} \quad (3)$$

$$n_s \equiv \text{total no. of turns} = \frac{d}{2(s + w)} \quad (4)$$

The web thickness (noted as ‘w’) and the space thickness (noted as ‘s’) are controlled by changing the height of the doctor blade in the tape-casting process and setting the thickness of the fugitive layer. The theoretical model predicts a pressure drop that is an order of magnitude higher than that measured. This is possibly due to the fact that the real microchannel has no walls at the open spaces, which are continuously linked. It should be noted, however, that the model assumes concentric circles. Foam-type catalysts are also known to have a good structure and achieve excellent mixing. On the other hand, foams cause a much higher (~10 times) pressure drop compared with the microchannel catalyst, given a similar open surface area, i.e., the physical surface area at the macro scale.

The stream is considered to maintain a laminar type of flow within the microchannel at the GHSV range employed in this work. The reactant gases may face the catalytic surface easily and will enhance the reforming reaction when mixing

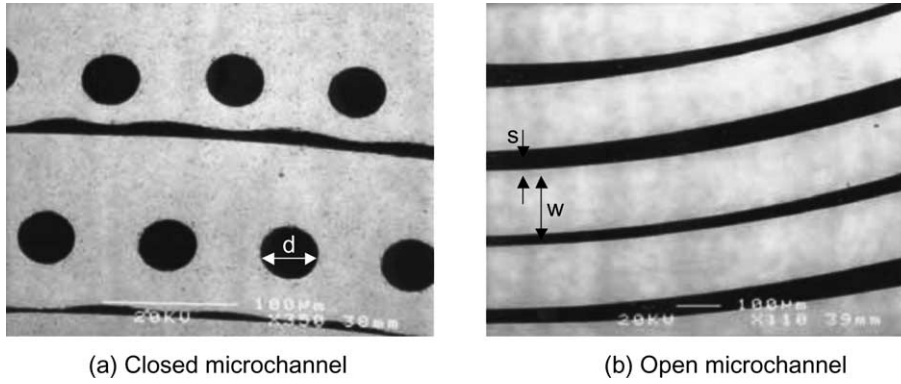


Fig. 5. Two different types of microchannels.

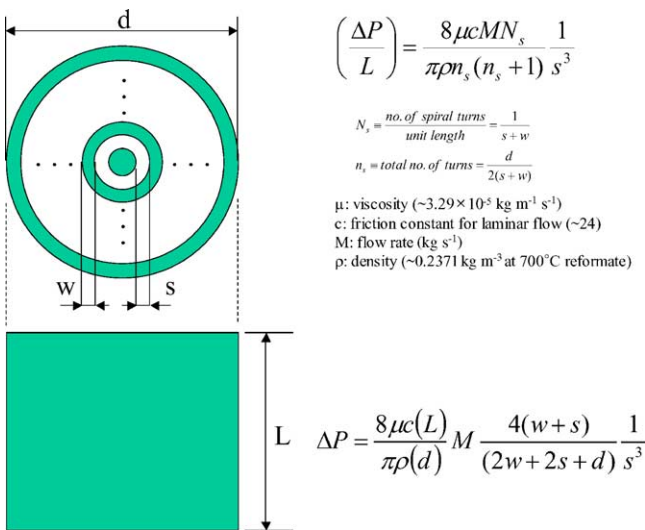


Fig. 6. Concentric model to calculate pressure drop at microchannel.

or turbulence exist in the channel space. An experimental configuration to investigate the mixing effect of gases in the channel space is shown in Fig. 7. A single piece of microchannel and two pieces of microchannels are loaded into a microreactor and the ATR performances are compared.

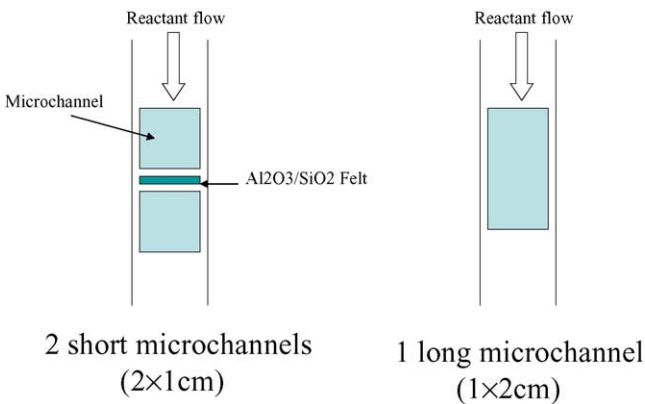


Fig. 7. Experimental configurations to investigate mixing effect at multiple microchannels.

Both of the experimental configurations have the same value of GHSV because they have the same catalytic volume when gas flow rates are kept the same. Thin aluminosilicate ($\text{Al}_2\text{O}_3/\text{SiO}_2$) felt, which was confirmed to be inert to the ATR reaction, was placed between two short microchannels to ensure desirable mixing of the gases. The hydrogen production rates in terms of mole of hydrogen per mole of provided iso-octane are shown in Fig. 8. The two experimental configurations give similar hydrogen production up to 3000 h^{-1} GHSV, and two short-microchannel configurations exhibit a higher hydrogen production rate than a long-microchannel configuration. This result can be explained in terms of a mixing effect in the space between the two short microchannels. Further experiments with three and four microchannels with same experimental set up have been performed but no more mixing effects are observed.

The microchannel ATR catalyst was scaled up for use in an engineering-scale fuel processor (10 KWe). The microchannel module with a special shuttle design for loading into a reactor with a diameter of 7 cm and a height of 2 cm is shown in Fig. 9. Two layers of microchannels were loaded inside the shuttle design to gain mixing effect mentioned above. These tests have demonstrated similar success in converting both gasoline-type fuels and natural gas.

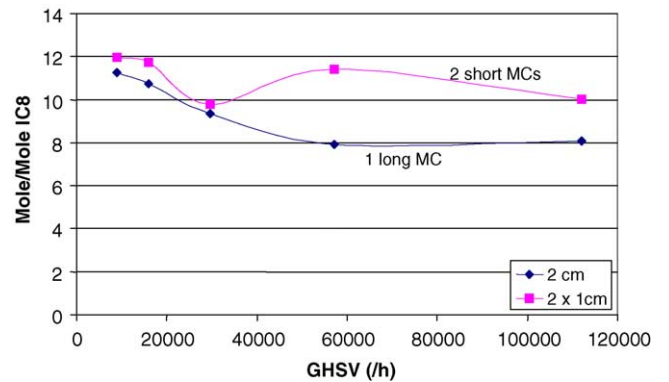


Fig. 8. Hydrogen production rates as mole hydrogen/mole iso-octane(IC8) supplied for single microchannel and two-microchannel configurations.

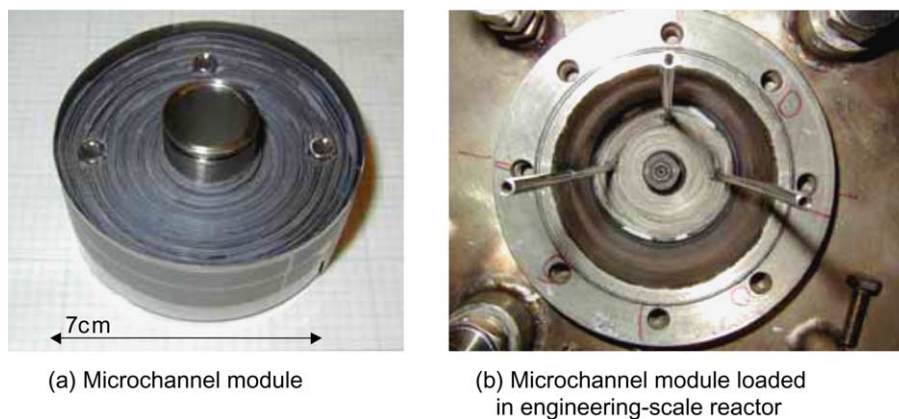


Fig. 9. Microchannel module for an engineering-scale (10 KWe) fuel processor.

4. Conclusions

A new concept of microchannel catalysts that are designed to accelerate mass-transport limited reactions has been developed at Argonne National Laboratory. Tested for the autothermal reforming of iso-octane, these structured catalysts exhibit excellent performance at space velocities approaching $250\,000\text{ h}^{-1}$, and at very low pressure drops. The microchannel catalysts perform much better than the pellet catalysts and can, therefore, dramatically decrease both the volume and the weight of the ATR reaction zones in the fuel processors.

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