

자동차탑재용 연료개질시스템을 위한 마이크로채널개발

Microchannel Development for Fuel Processor of Automotive Applications

배중면
한국과학기술원 기계공학과

Abstract

Fuel processing is an enabling technology for faster commercialization under lack of hydrogen infrastructures. It has been reported that the development of novel catalysts that are active and selective for hydrocarbon reforming reactions. It has been realized, however, that with pellet or conventional honeycomb catalysts, the reforming process is mass transport limited. This paper reports the development of catalyst structures with microchannels that are able to reduce the diffusion resistance and thereby achieve the same production rate within a smaller reactor bed. These microchannel reforming catalysts were prepared and tested with natural gas and gasoline-type fuels in a microreactor (1-cm dia.) at space velocities of up to 250,000 per hour. These catalysts have also been used in engineering-scale reactors (10 kWe, 7-cm dia.) with similar product qualities. Compared to pellet catalysts, the microchannel catalysts enable a nearly 5-fold reduction in catalyst weight and volume.

1. Introduction

Proton exchange membrane fuel cells (PEMFC) are being developed for electric power generation in a variety of applications that include transportation, stationary, military, portable, etc. The PEMFC produces electricity by electrochemically oxidizing hydrogen. However, in the absence of a hydrogen refueling infrastructure, the successful commercialization of PEMFC systems in many applications will depend upon the ability to convert currently available fuels into hydrogen (of PEMFC acceptable purity level.)

Production of hydrogen in chemical industry is a well-established process. The three major approaches for the conversion of hydrocarbon fuels to hydrogen are steam reforming, partial oxidation, and autothermal reforming a combination of steam reforming and partial oxidation. Argonne National Laboratory has discussed the advantages of the autothermal reforming (ATR) process for many applications which face constraints on size, weight, duty cycle, etc., such as in automotive power plants[. R. Kumar, S. Ahmed, M. Krumpelt, and K.M. Myles, "Improved fuel cell system for transportation application," U.S. Patent 5,248,566, 1993.]. In the ATR process, fuel is co-fed with steam and air, and the feed composition is adjusted to maintain a slightly exothermic reaction.

Figure 1 plots the thermodynamic equilibrium gas compositions from the autothermal

reforming of iso-octane, and shows that the hydrogen concentration peaks at 700C, which thus represents a preferred operating temperature[. S. Ahmed, R. Doshi, R. Kumar, and M. Krumpelt, "Gasoline to hydrogen-a new route for fuel cells," Electric and hybrid vehicle technology '97, p.77, UK and international press, Dorking, Surrey, RH42EU, UK, 1997.]. To enable the fuel reforming process to occur at about 700C, Argonne National Laboratory has developed a novel ATR catalyst system, which has been found to be very active, effective for the conversion of various carbonaceous fuels, and has shown excellent resistance to sulfur and coking[. M. Krumpelt, S. Ahmed, R. Kumar, and R. Doshi, "Method for making hydrogen-rich gas from hydrocarbon fuel," U.S. Patent 5,929,286][. J. Kopasz, D. Applegate, L. Ruscic, S. Ahmed, and M. Krumpelt, "Effects of gasoline components on fuel processing and implications for fuel cells," Abstract, 2000 Fuel cell seminar, pp. 284-287]. Indeed, the intrinsic rates for conversion of hydrocarbons to hydrogen are fast enough that with pellet catalysts the overall rate is limited by mass transport limitations.

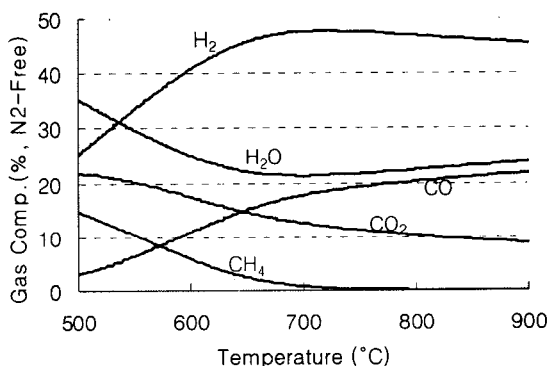


Figure 1. Equilibrium product gas composition vs. temperature, calculated for the reaction between iso-octane (C₈H₁₈), air (O₂/C₈=3.71), and water (H₂O/C₈=9.11).

Recognizing 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 provides great control over the geometric dimensions.

2. Experiments

2-1. Fabrication

The structured microchannel ATR catalyst is fabricated using a modified ceramic tape casting process. In this work we used Gd-doped CeO₂ with 0.5wt.% Pt (CGO-Pt) as the catalyst material, since it has demonstrated excellent activity for the desired reforming reaction. Catalyst

powders with 5-50 m/g of specific surface area can be used. The powders are dispersed by using commercial dispersion agents and solvents, such as xylenes or alcohols. The dispersed catalyst slurry is mixed with organic binder resins such as poly vinyl butyral or acryloid. The final slurry is cast at the desirable thickness (50-200 μm) with a doctor blade and subsequently dried in air. Fugitive materials such as organic fabric can be inserted while the tape keeps slurry phase to leave holes or thin fugitive materials (1 ~ 50 μm) can be added on top of fully dried catalyst tape to leave space after the burning process. The dried catalyst tape maintains flexibility due to plasticity of organic binder system and enables further mechanical treatment such as cutting and rolling. The tape is cut to strips of about 1-cm width and rolled to a so-called jellyroll shape of the desired diameter. Figure 2 shows a small size microchannel catalyst of about 1-cm diameter for microreactor tests. The microchannel is 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 are created.

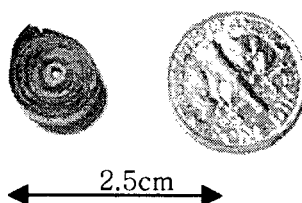


Figure 2. Microchannel catalyst used for ATR tests in microreactors (1-cm dia.)

2-2. Characterization of microchannel catalyst

After loading a microchannel in the green state into the microreactor tube, a special heat treatment was carried out 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 the sintering at a higher (>500C) temperature.

The activity of the microchannel catalysts was studied in the microreactor under varying operating [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 followed by vaporization at about 150C. The air rate was controlled with a mass flow controller. The GHSV was calculated based on the volume of reactants in the gas phase at 25C. The reactor temperature was controlled between 600-900C, 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 with the help of a gas chromatograph attached with mass spectrometer (HP 6890/HP 5973) after de-humidification of the gases.

3. Experimental Results and Discussions

Figure 3 shows the concentrations (on a nitrogen and water free basis) of hydrogen and byproduct hydrocarbons in the product stream from the microreactor, as a function of the space velocity. It should be noted that the "H₂ after WGS" refers to the concentration of hydrogen that would result if the carbon monoxide formed during the reforming reaction were to be converted to additional hydrogen via the water gas shift reaction ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$). For these experiments the furnace was set at 650C, and the feed proportions were adjusted to maintain $\text{O}_2/\text{C}_8 = 3.7$ and $\text{H}_2\text{O}/\text{C}_8 = 9.1$.

Thermodynamic equilibrium calculations suggest that at 650C, the product gas should contain 68.7% hydrogen on a dry, nitrogen-free basis. As the plot shows, the microchannel was able to maintain high yields, comparing favorably to the equilibrium level, at space velocities (GHSV) approaching ~250,000 /hr. The concentration of hydrocarbons (such as CH₄) in the product gas shows an inverse correlation with the hydrogen curve. This is to be expected since each mol of byproduct hydrocarbon significantly reduces the hydrogen yield, e.g., each mol of methane can be reformed to yield 4 mols of hydrogen.

Figure 4 compares the hydrogen yields (before WGS) achieved with pellet catalysts and the microchannel catalysts. It is evident that the microchannel catalyst outperformed the pellet catalyst, supporting the hypothesis that the microchannel structured catalyst reduces the mass transport limitations. The advantage of the microchannel structure is especially true at the higher processing rates.

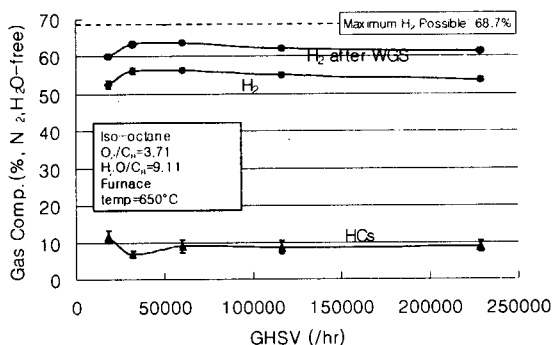


Figure 3. Conversion characteristics of microchannel catalyst of iso-octane ATR reaction.

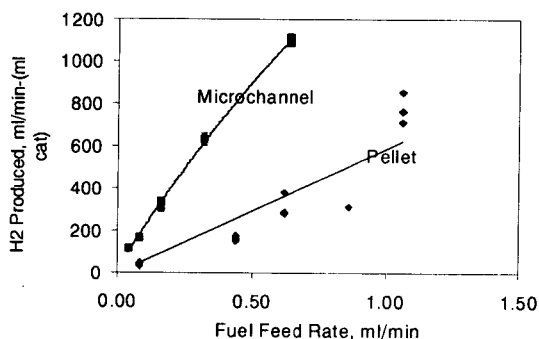


Figure 4. Comparison of ATR microchannel and pellet-type ATR catalysts for iso-octane as a function of fuel feed rate.

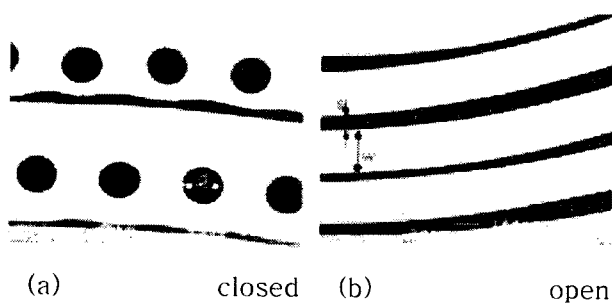


Figure 5. Two different types of microchannels.

Void diameter (d) and thickness (s) are controlled by changing fugitive materials. In order to address the effect of the channel design on the pressure drop, two types of microchannels were fabricated and studied. Figure 5 shows a scanning electron micrograph of two different types of microchannels. Figure 5(a) is a "closed" microchannel and 5(b) is an "open" microchannel. The diameter of the void (noted as ' d ') in figure 5(a) and the void thickness (noted as ' s ') in figure 5(b) can be easily controlled by using different diameter or thickness of fugitive materials, with void thicknesses of the order of 1 μm being easily achieved. Such dimensions are not possible in commercially available honeycomb-type cordierite supports. The open-type microchannel exhibited very low pressure drop in our study. A simple model (Figure 6) was established to estimate the pressure drop.

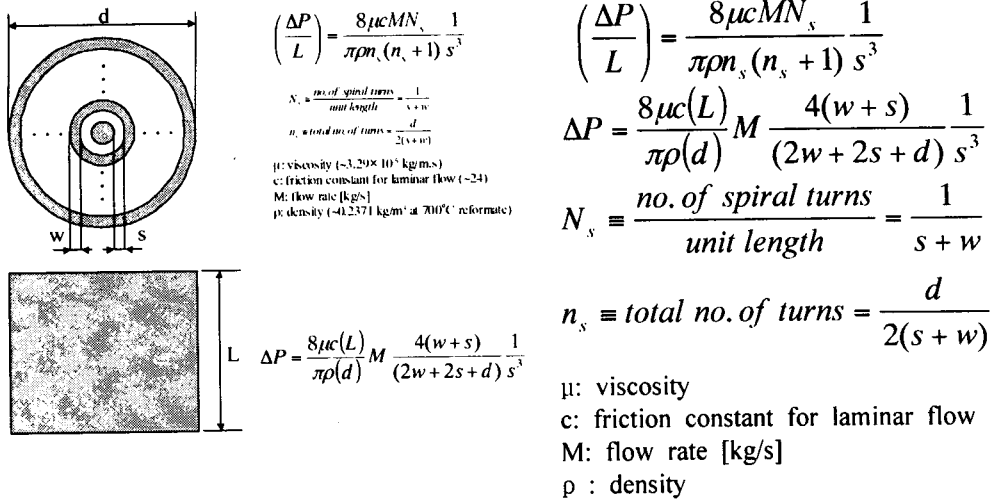


Figure 6. Concentric model to calculate pressure drop at microchannel.

The web thickness (noted as 'w') and space thickness (noted as 's') are controlled by changing the height of the doctor blade for the tape casting process and setting the thickness of the fugitive layer. The theoretical model predicted a pressure drop that was an order of magnitude higher than that measured and it possibly due to the fact that the real microchannel has no walls at the open spaces, which are continuously linked. However, the model assumed concentric circles.

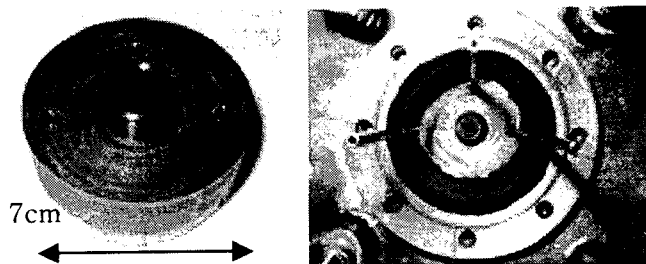


Figure 7. Microchannel module for an engineering-scale (10 KWe) fuel processor.

Foam type catalysts are also known to be good structure achieving good mixing. However, the foams cause much higher (~10 times) pressure drop compared to this microchannel catalyst, assuming similar open surface area, i.e., the physical surface area at macro scale. The microchannel ATR catalyst was scaled up for use in an engineering-scale fuel processor (10 KWe). Figure 7 shows the microchannel module with a special shuttle design for loading into a reactor with a diameter of 7-cm and 2-cm high. These tests showed similar successes in converting both gasoline-type fuels and natural gas.

4. Conclusions

A new concept of microchannel catalysts 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 exhibited excellent performance at space velocities approaching 250,000 per hour, and at very low pressure drops. The microchannel catalysts performed much better than pellet catalysts and can, therefore, dramatically decrease the volume and weight of ATR reaction zones in fuel processors.

References

1. R. Kumar, S. Ahmed, M. Krumpelt, and K.M. Myles, "Improved fuel cell system for transportation application," U.S. Patent 5,248,566, 1993.
2. S. Ahmed, R. Doshi, R. Kumar, and M. Krumpelt, "Gasoline to hydrogen-a new route for fuel cells," Electric and hybrid vehicle technology '97, p.77, UK and international press, Dorking, Surrey, RH42EU, UK, 1997.
3. M. Krumpelt, S. Ahmed, R. Kumar, and R. Doshi, "Method for making hydrogen-rich gas from hydrocarbon fuel," U.S. Patent 5,929,286
4. J. Kopasz, D. Applegate, L. Ruscic, S. Ahmed, and M. Krumpelt, "Effects of gasoline components on fuel processing and implications for fuel cells," Abstract, 2000 Fuel cell seminar, pp. 284-2