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Performance of microchannel reactor combined with combustor for methanol steam reforming

Jung Yeon Won, Hee Kwon Jun, Min Ku Jeon, Seong Ihl Woo *

Department of Chemical and Biomolecular Engineering, Center for Ultramicrochemical Process Systems,
Korea Advanced Institute of Science and Technology, 373-1 Guseong-dong, Yuseong-gu Daejeon 305-701, Republic of Korea

Abstract

The microchannel reactor with combustor for methanol steam reforming was fabricated to produce hydrogen for onboard proton exchange membrane (PEM) fuel cell device. A commercial copper-containing catalyst ($Cu/ZnO/Al_2O_3$) and Pt/ZrO_2 were used as a catalyst for methanol steam reforming and combustion reaction, respectively. It was found that catalyst layer with zirconia sol solution in microchannel showed no crack on the surface of catalyst layer and an excellent adherence to stainless steel microchannel even after reaction. The temperature of combustor could be controlled between 200 and 300 °C depending on the methanol feed rate. The hydrogen flow of $3.9\,\mathrm{l\,h^{-1}}$ hydrogen was obtained with the reforming feed flow rate of $3.65\,\mathrm{ml\,h^{-1}}$ at 270 °C.

Keywords: Hydrogen; Microreactor; Reforming; Methanol; Combustion

1. Introduction

The fuel cell technology is considered as an attractive alternative because of its environmental compatibility and high energy conversion efficiency [1]. Among the various types of fuel cells, polymer electrolyte fuel cell (PEMFC) systems are widely studied for portable electric devices because PEMFC provides the necessary specific power, power density and durability to replace lithium-ion batteries [2,3]. Although there is a trouble to store and transport hydrogen, it is preferred for portable PEM fuel cell. Furthermore, it is difficult to make small hydrogen storage tanks for application in portable PEMFC. Therefore, onboard fuel processing is an inevitable choice.

Technology for producing hydrogen-rich gas from hydrocarbon is based on three different catalytic processes, i.e., thermal decomposition, partial oxidation and steam reforming [4–8]. Methanol steam reforming (SRM), among these processes, provides high hydrogen concentration and low carbon monoxide concentration. The three key reactions of SRM can be written by the following equations [9–11]:

$$CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2 \quad \Delta H^\circ_{298} = +49.4\,\mathrm{kJ\,mol^{-1}} \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^\circ_{298} = -41.1\,\mathrm{kJ\,mol^{-1}} \tag{2}$$

$$CH_3OH \leftrightarrow CO + 2H_2 \quad \Delta H^\circ_{298} = +90.0\,\mathrm{kJ\,mol^{-1}} \tag{3}$$

The SRM reaction is somewhat endothermic as indicated above. Moreover, in order to use fuel processor for portable device, the temperature of reformer should be maintained above 200 °C. At this condition, microstructured reactors are preferable because of their fast heat transfer. Microreactors have various advantages like small size and light weight for application in portable fuel cell system [12–14]. At the same time microreactor shows low heat and mass transfer resistances and allows chemical reactions to proceed at much higher rates.

Seo et al. [13] developed microfuel processor with a vaporizer and a reformer for PEM fuel cells. The dimension of reformer was 70 mm × 40 mm × 30 mm. Electric heat source provided heat for the endothermic reaction. The developed micro-reformer generated power output of 10 W. Also, Cremers et al. [15] investigated microstructured-reactor system consisting of stainless steel plates with 62 microchannels. The

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* Corresponding author. Tel.: +82 42 869 3918; fax: +82 42 869 8890.
E-mail address: siwoo@kaist.ac.kr (S.I. Woo).

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reformer with 15.9 g of C18—HA methanol synthesis catalyst was operated at the temperature range of 250–270 °C. In the composition of 43.6% water, 36.4% methanol and 20% nitrogen, conversion higher than 90% was obtained in weight hourly space velocities (WHSV) of 12.5 h^{-1}.

In this study, we developed a microchannel reactor with combustor in the backside. This reactor was designed to supply the sufficient heat for the endothermic reaction. Commercial $Cu/ZnO/Al_2O_3$ catalyst and Pt/ZrO_2 catalyst were used for the SRM and the combustion reaction, respectively. Performance of reformer with combustor was evaluated under various reformer conditions.

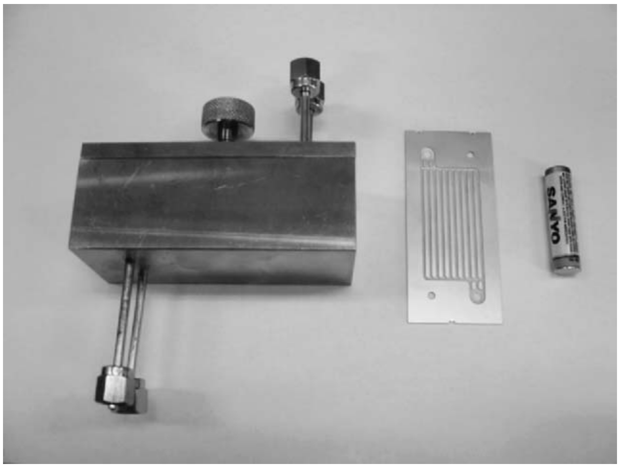

Fig. 1. Photograph of CH_3OH reformer with combustor.

2. Experimental

2.1. Preparation of catalyst

A commercial $Cu/ZnO/Al_2O_3$ (ICI 33-5, CuO 50%, ZnO 33%, Al_2O_3 8% and BET surface area = 66 $m^2\ g^{-1}$) catalyst was used for the SRM. Two weight percent Pt/ZrO_2 as a combustion catalyst was prepared by an impregnation method. ZrO_2 (BET surface area = 4.9 $m^2\ g^{-1}$ and 0.25 mm in diameter, Sigma) was impregnated by using an aqueous solution of tetraammine platinum(II) nitrate (Strem). The catalyst was dried in an oven at 110 °C for 2 h. To eliminate the undesired species, the catalyst was calcined in air at 500 °C for 2 h.

2.2. Catalyst coating

The zirconia sol was prepared by adding HNO_3 (HNO_3:Zr = 1:2) to a zirconium isopropoxide isopropanol complex (Aldrich, 99%). Zirconia powder was mixed with zirconia sol and isopropanol was added to adjust viscosity of zirconia sol solution. In order to enhance the adhesion between catalyst and substrate, zirconia sol solution was undercoated on microchannel. Reforming catalyst slurry was obtained by mixing 0.2 g $Cu/ZnO/Al_2O_3$ catalyst with 1 ml zirconia sol solution and 1 ml isopropanol. Combustion catalyst slurry was also prepared in the same way. After ball-milling for 12 h, catalyst slurries were coated on undercoated zirconia layer and dried at 70 °C for 6 h. This process was repeated to give the desired amount of catalyst. Stainless steel substrate coated with catalyst was calcined at 350–400 °C to increase adhesion between catalyst and microchannel.

2.3. Microchannel reactor design

Substrates with microchannels were fabricated with etching process. The dimension of the plate was 80 mm long, 35.5 mm wide, 1 mm thick. The plate contains 10 channels of 45 mm long, 1 mm wide, and 0.5 mm deep. Three substrates coated with steam reforming catalyst and combustion catalyst were stacked inside housing (Fig. 1). The loading of reforming catalyst ($Cu/ZnO/Al_2O_3$) and combustion catalyst (Pt/ZrO_2) was 0.096 and 0.066 g, respectively. To exchange heat

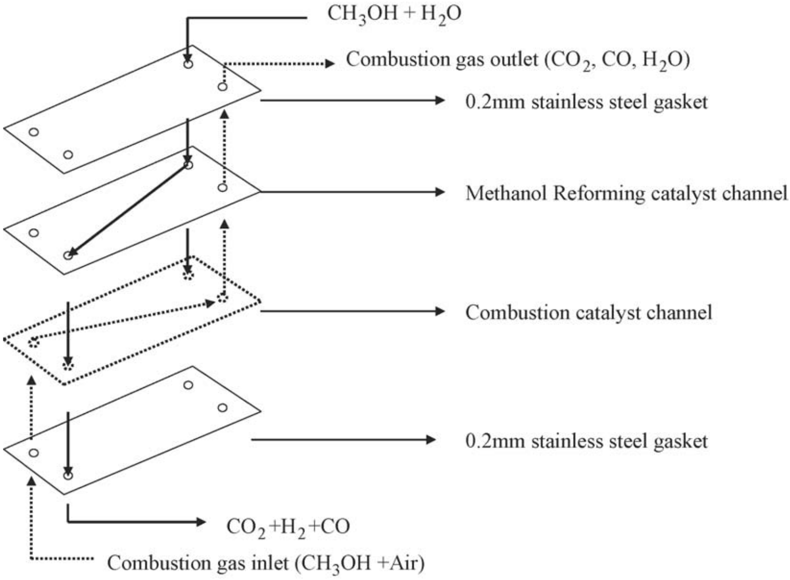

Fig. 2. Flow distribution of products and reactants inside micro-reformer with combustor.

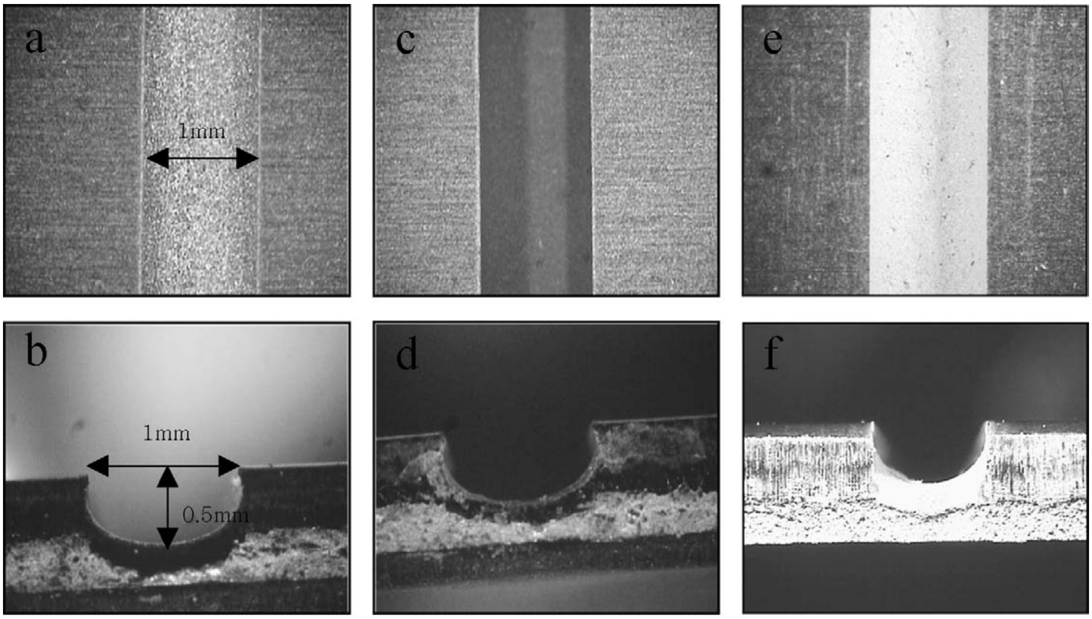

Fig. 3. Images of microchannel after coating zirconia and catalyst on the microchannel: (a) before coating, top view; (b) before coating, cross-section view; (c) $Cu/ZnO/Al_2O_3$, top view; (d) $Cu/ZnO/Al_2O_3$, cross-section view; (e) Pt/ZrO_2, top view; (f) Pt/ZrO_2, cross-section view.

effectively, the microchannels coated with combustion catalyst were placed on the backside of microchannels with reforming catalyst. The flow patterns of reactants and products for each reactions are shown in Fig. 2. Four thermocouples were located at inlet and outlet of each gas flows to measure the temperature.

2.4. Combustion and reforming reaction

Two feed lines were installed for combustion and reforming reaction. Methanol and methanol/water mixture were supplied to the combustion and reforming reactor by using syringe pumps with carrier gas (air and helium) and the temperature of feed line was heated above 100 °C to prevent condensation of methanol. The feed rate of liquid was controlled between 3.2 and 5.5 ml h^{-1} for combustion and 1.65 and 3.65 ml h^{-1} for SRM, respectively.

The product gas was consisted of H_2, CO_2, CO, N_2, CH_3OH and H_2O. Gas stream was passed through a cold trap to remove liquid components and fed into on-line gas chromatograph for analysis of H_2, CO and CO_2.

3. Results and discussion

3.1. Catalyst coating

For catalytic applications, the catalyst layer on the microchannels should be adhered strongly. In order to increase adhesion between the catalyst layer and the substrate, porous supports such as SiO_2 or Al_2O_3 were coated on the microchannels [16]. In this study, ZrO_2 layer was coated on microchannels to improve adhesion between catalyst layer and substrate. Dilute ZrO_2 sol solution was used to synthesize ZrO_2 layer. Lim et al. reported that the dilute ZrO_2 sol solution was better than high concentrated one to obtain uniform oxide layer [12]. Therefore, ZrO_2 sol solution was diluted to adjust proper viscosity by isopropyl alcohol. After coating combustion and reforming catalyst on the surface of microchannel with a syringe, the images of catalyst layer are shown in Fig. 3. It was found that there is no crack on the catalyst layers even after ultra sonic treatment for 1 h. Fig. 4 shows a sample of substrate

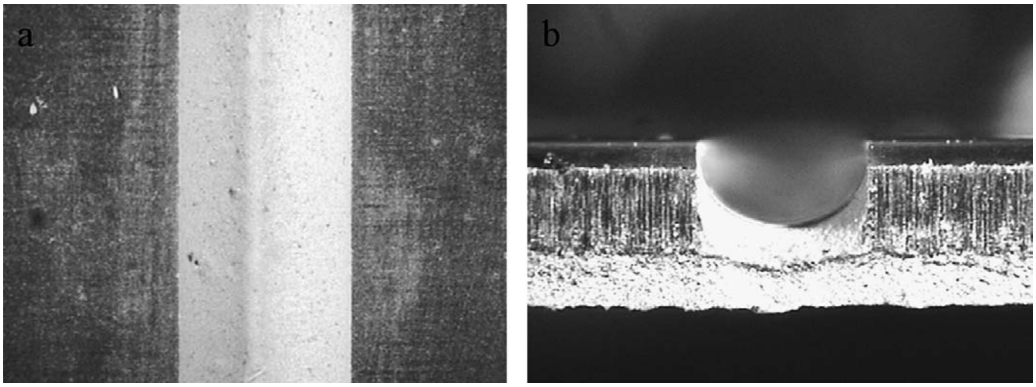

Fig. 4. Images of Pt/ZrO_2 catalyst layer after combustion reaction for 72 h: (a) top view; (b) cross-section view.

coated with the Pt/ZrO_2 catalyst after combustion reaction for 72 h. Cracks and separation of Pt/ZrO_2 catalyst layer from substrate were not observed indicating that an excellent adhesion between the catalyst layer and the microchannel was maintained.

3.2. Performance of combustor

The first issue to examine is the performance of the combustor for supplying heat to methanol steam reforming. Therefore, only three plates coated with 0.066 g combustion catalyst were stacked in housing and investigated without methanol steam reforming. The time on stream combustion reaction with housing is shown in Fig. 5. At room temperature, the temperature of the combustor did not rise because the rate of heat dissipation is much larger than that of heat generation and the thermal capacity of housing is too large to elevate the temperature. In order to overcome the barrier of ignition, heat was introduced with electric heater. Electric heat was turned off around 110 °C and the methanol–air mixture was introduced to the combustor. In contrast to the case without pre-heating, temperature of the combustor was increased slowly due to large thermal capacity of housing. The time at which micro-reformer gets to operating temperature is mainly a function of the air/methanol feed rate. In this system, with methanol feed rate for combustion of 0.063–0.07 $cm^3\ min^{-1}$, it took 450 min for the temperature increased from 120 to 240 °C, at which the methanol steam reforming takes place actively. This result confirms the ability for micro-reformer to elevate temperature without any external heating. If the stacking technology is substituted into laser welding, brazing and diffusion bonding method and if material of the substrate is changed into material which has low thermal capacity such as aluminum, the heating capacity of the micro-reformer will decrease significantly, which will greatly improve the dynamics of microchannel reactor.

In order to provide heat for the endothermic methanol steam reforming, the performance of combustor was evaluated at various flow rates of combustion reactant as shown in Fig. 6. Even though the feed rate of methanol was increased, the conversion of methanol was maintained higher than 95%. Heat of reaction (916 $J\ min^{-1}$) was obtained at total flow rate (gas phase) of 300 $cm^3\ min^{-1}$. In our system, heat required for the endothermic reaction is 16 $J\ min^{-1}$ for the endothermic reaction when feed rate of methanol is 0.0275 $cm^3\ min^{-1}$ and H_2O/CH_3OH molar ratio is 1.5. The performance of combustor producing heat at the rate of 916 $J\ min^{-1}$ is sufficient for supplying heat for methanol steam reforming reaction.

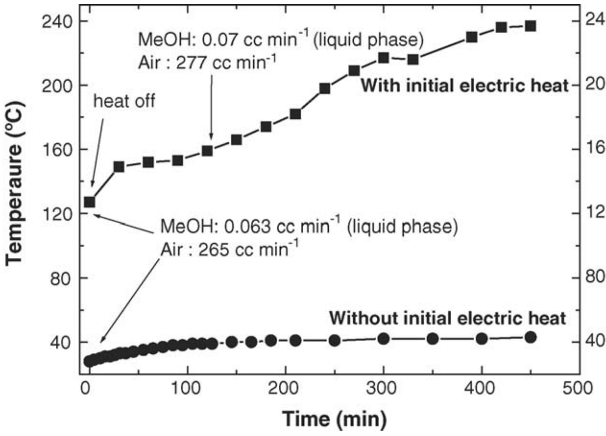

Fig. 5. Temperature profiles as a function of time ($O_2/CH_3OH = 1.5$).

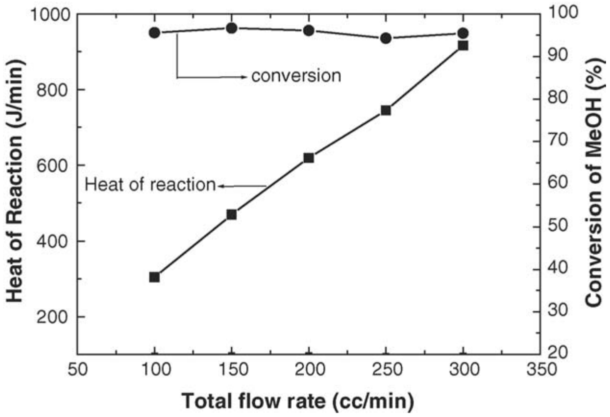

Fig. 6. Effect of combustion reactant flow rate on the generation of heat (catalyst loading = 0.066 g, $O_2/CH_3OH = 1.5$, reaction temperature = 270 °C).

3.3. Performance of micro-reformer with combustor

Based on the results of the combustor, micro-reformer with the combustor was investigated. Each three microchannel plates coated with reforming and combustion catalyst were stacked. Fig. 7 shows temperature variations at the inlet and outlet of reformer and combustor unit according to the methanol feed rate for the combustion reaction. The temperature of microchannel reactor could be controlled and maintained in the range of methanol feed rate between 3.2 and 5.5 $ml\ h^{-1}$. Temperature deviations in microreactor were within ±6 °C between inlet and outlet gas flows. Temperature

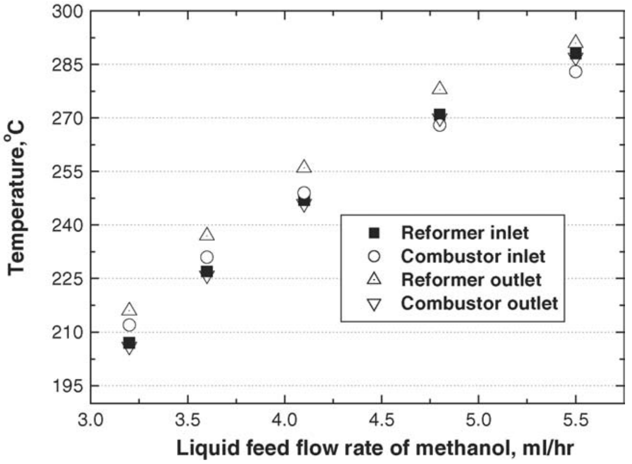

Fig. 7. Temperature variations at the inlet and outlet of reformer and combustor channel (O_2/CH_3OH molar ratio = 1.5, H_2O/CH_3OH molar ratio = 1.5).

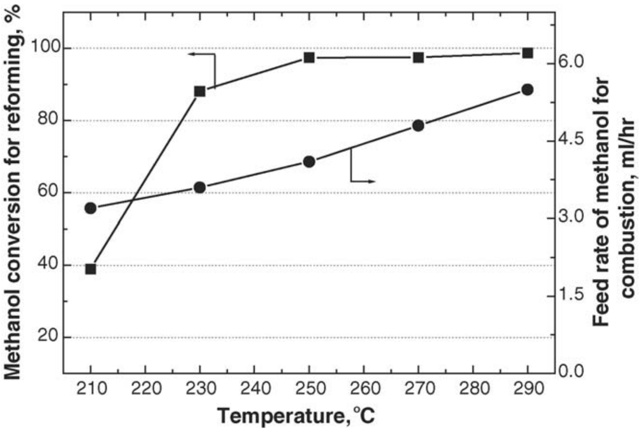

Fig. 8. Methanol conversion as a function of reaction temperature (liquid feed rate for reforming = 1.65 ml h^{-1}, H_2O/CH_3OH molar ratio = 1.5).

increased linearly with the increase in the liquid flow rate of methanol.

Performance of the micro-reformer with the combustor was evaluated, as shown in Fig. 8. The methanol conversion for reforming was increased with increasing reaction temperature. The methanol conversion over 90% was achieved at between 250 and 290 °C with a constant feed flow rate of 1.65 ml h^{-1}. The composition of reformate gas and hydrogen generation rate at various temperatures is shown in Fig. 9. As the temperature was increased from 210 to 250 °C, hydrogen generation rate greatly increased from 0.8 to 1.9 l h^{-1}. The highest hydrogen production rate of 1.9 l h^{-1} was obtained between 250 and 290 °C. This result corresponds to 2.7 W of power output at the operating condition of 60% efficiency of fuel cell and at the 80% utilization of H_2. The concentration of hydrogen was between 76 and 79%. As the reaction temperature was increased from 210 to 290 °C, the CO concentration increased from 1.2 to 1.4%. This is due to the reverse water–gas shift reaction. For application in fuel cell, CO concentration should be less than 10 ppm which can be done at CO oxidation reactor. Among the various ways of CO clean-up, PROX is one of the most effective methods. Chen et al. [14] developed the microchannel reactor for PROX system and reported that 99.5% conversion of CO was achieved with 10 000 ppm CO (GHSV = 100 000 h^{-1}, O_2/CO = 1, and temperature from 180 to 220 °C).

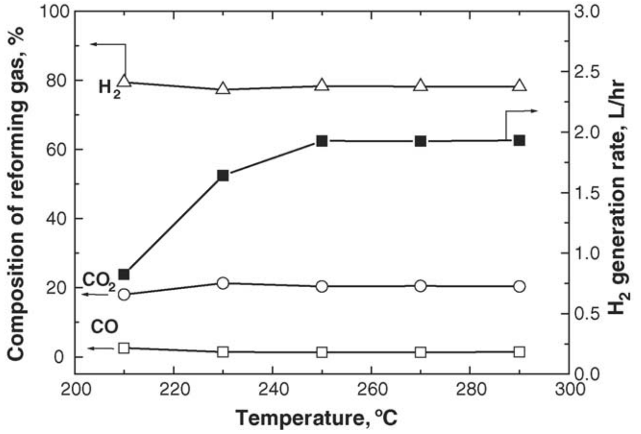

Fig. 9. Composition of reformate gas and H_2 generation rate at various reaction temperature (feed rate for reforming = 1.65 ml h^{-1}, H_2O/CH_3OH = 1.5).

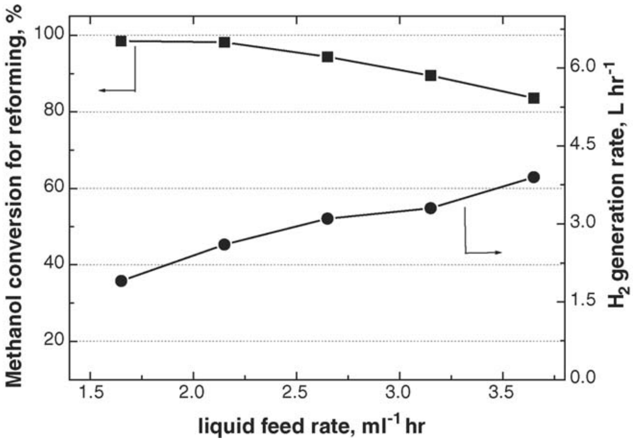

Fig. 10. Performance of micro-reformer at various feed rates for reforming (reaction temperature = 270 °C, H_2O/CH_3OH molar ratio = 1.5).

In order to measure the maximum performance of reformer, methanol steam reforming was investigated at feed rate between 2.15 and 3.65 ml h^{-1}, as shown in Fig. 10. The steam to carbon mole ratio was kept constant at 1.5. The hydrogen generation rate was increased with increasing feed rate, while the conversion of methanol was decreased. The maximum hydrogen producing rate of 3.9 l h^{-1} was obtained at 270 °C with a feed rate of 3.65 ml h^{-1} and methanol conversion was higher than 80%.

4. Conclusions

A microchannel reactor with combustor was designed for methanol steam reforming. The catalyst layer with dilute ZrO_2 sol solution showed an excellent adhesion even under blowing gas flow condition. The combustor performance could be controlled and maintained in the temperature range of 210–290 °C. Temperature profiles of inlet and outlet of each gas flow were also investigated. The hydrogen of 3.9 l h^{-1} was obtained at the feed flow rate of 3.65 ml h^{-1} at 270 °C and this result corresponded to the generating of hydrogen for power output of 5.5 W.

Acknowledgement

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