

# Silicon-based miniaturized reformer with methanol catalytic burner

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## Abstract

Silicon fabrication technologies such as a photolithography, a wet chemical etching and an anodic bonding were introduced to form micro-channel on silicon wafer. Pt–Al<sub>2</sub>O<sub>3</sub> (5 wt%, Johnson Matthey) was loaded into the micro-channel to perform methanol oxidation reaction that is highly exothermic. The methanol oxidation reaction occurring in the micro-channel was investigated, and the heat of reaction and conversion were evaluated under various pretreatment experimental conditions. The methanol oxidation reaction occurring over layer type catalyst in the micro-channel showed the conversion over 90%, fast start-up and accurate temperature control.

After testing the performance of a miniaturized methanol catalytic burner (MCB) separately, it was applied to a reformer as a heat source, and the performance of the reformer was analyzed. The temperature of a reformer-MCB stack consisting of three reformers and two MCBs was successfully controlled only with the MCB without the support of the electric heater. The stack produced 73% hydrogen and 5000 ppm CO with the methanol conversion of 65%.

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## 1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have received much attention due to their high energy density and environmentally friendly characteristic. However, there are many barriers which prevent the commercialization of PEMFC. One of the barriers is the fuel. Hydrogen that is gaseous phase in ambient condition causes the problem in storage and supply. As a solution, the compressed hydrogen has been recommended, however, it is not applicable to portable use because small space is available for hydrogen storage in portable system. Thus the reforming system got an attention as a fuel supplying method for the portable application of the PEMFC instead of compressed hydrogen. Hydrogen generation from the methanol was highlighted because of a high hydrogen to carbon ratio, an absence of carbon–carbon bond and a potentially high production capacity [1,2].

There are various ways of generating hydrogen from methanol such as a methanol decomposition, a partial oxidation of methanol and a steam reforming of methanol (SRM). But the methanol decomposition and the partial oxidation of methanol are not favorable because of high CO concentration and low hydrogen yield, respectively. Thus the SRM reaction that has high hydrogen yield as well as low CO concentration has been adopted as a reforming reaction. The disadvantage of SRM reaction is that it requires an external heat source because it is a highly endothermic reaction [3,4].

The electrical heating methods like a heating rod or a thin film heater have been introduced to elevate the temperature of the miniaturized reformer [5–8]. However, it is a paradox to use electric energy to generate hydrogen that is used for the generation of electric energy at the fuel cell. Thus the chemical reaction of fuel combustion has been studied. The substitution of the electric heater with a catalytic burner makes the reformer system self-sustainable. Catalytic burner uses various fuels such as hydrogen and hydrocarbons (methane, ethane, propane, butane and methanol) [9–13]. The miniaturized methanol catalytic burner (MCB), that is not only easy to handle but also available for the miniaturized methanol reformer, was investigated in this study.

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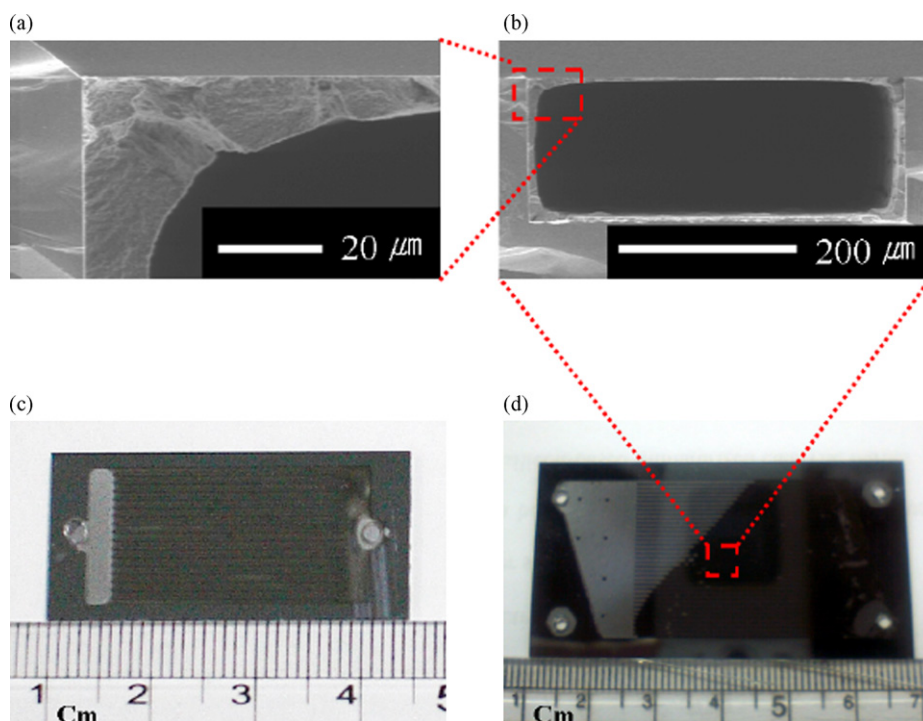
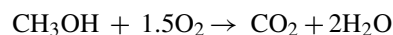


Fig. 1. (a) Enlargement of (b); (b) FESEM image of catalyst coating profile; (c) photoimage of methanol catalytic burner; (d) photoimage of methanol catalytic burner for the stack.

A miniaturized catalytic burner was fabricated using micro electro mechanical system (MEMS) technology. Commercial platinum catalyst was applied for the total oxidation of methanol (1).



$$\Delta H_{280^\circ\text{C}} = -673.2 \text{ kJ/mol} \quad (1)$$

A self-ignition characteristic and the durability of the miniaturized catalytic burner were analyzed varying the experimental conditions. Its usefulness was tested by measuring the performance of the reformer integrated with the catalytic burner.

## 2. Experiment

### 2.1. The fabrication of a catalytic burner

(110) Silicon wafer and Pyrex<sup>TM</sup> (#7740, corning) were introduced to the reactor fabrication by using silicon fabrication technologies such as a photolithography, a wet chemical etching and an anodic bonding. Following the formation of micro-channels by using an anisotropic wet etching, an etched silicon wafer was bonded with Pyrex<sup>TM</sup> by the anodic bonding [5]. Through this process, two types of catalytic burners were fabricated as shown in Fig. 1(c) and (d). One was for the test of catalytic burner itself, and the other was for the stack integration test with the reformer. The catalytic burner for the performance characterization had 17 parallel micro-channel of 24 mm in length, 600 μm in width and 240 μm in depth, and the burner for integration had 36 parallel micro-channels with 32 mm long, 600 μm wide and 240 μm deep. Two types of

reformers were also fabricated. One was for integration test with the catalytic burner and the other was for a reformer-burner stack. The reformer for integration test had 350 mm serpentine channel and it for the stack had four serpentine channels with 288 mm long.

After finishing the fabrication of the burner and the reformer, both reactors were annealed to form a SiO<sub>2</sub> adhesion layer. Then a Pt–Al<sub>2</sub>O<sub>3</sub> (5 wt%, Johnson Matthey) catalyst and a commercial Cu–ZnO–Al<sub>2</sub>O<sub>3</sub> (MDC-3, Süd-Chemie) catalyst were coated inside or micro-channel of catalytic burner and reformer by a fill-and-dry coating method [14]. Fig. 1(a) and (b) shows the field emission scanning electron microscope (FESEM) image of Pt–Al<sub>2</sub>O<sub>3</sub> catalyst coating profile. Twenty-seven milligrams of Pt–Al<sub>2</sub>O<sub>3</sub> catalyst was coated inside of catalytic burner independent of the design and the purpose. The reformer also had the same amount of catalyst of 20 mg inside of micro-channel apart from the design and the purpose. After catalyst coating, a thin film heater was deposited by a direct current (dc) magnetron sputtering on the silicon side of the catalytic burner to control the temperature of the burner during catalyst pretreatment, self-ignition experiment and the start-up of reformer-catalytic burner stack. The thin film heater was composed of three components of a tantalum nitride (TaN<sub>x</sub>) heating material, a tantalum adhesion layer and a gold contact pad.

### 2.2. Experimental setup

Fig. 2 shows a schematic diagram of the experimental setup for the characterization of the catalytic burner. The temperature controller was composed of a relay (LG, RY5W-K) and a LM324 (Britestone, LM324NG), and its control software

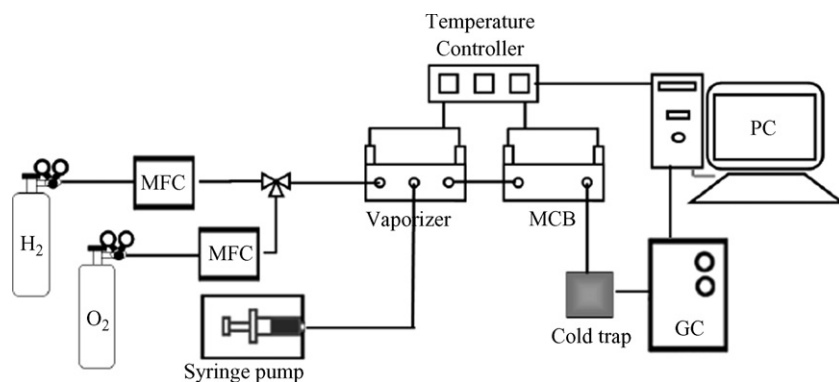


Fig. 2. Experimental setup.

that was programmed by LabVIEW™ to record experimental parameters such as time, temperature and relay-on-time. A syringe pump (KDS100) fed methanol into the catalytic burner through a vaporizer, and the oxygen was supplied by a mass flow controller (MFC). Methanol and oxygen were mixed in the vaporizer, and then entered into the catalytic burner. The gas production rate was measured with a digital bubble flow meter and gas composition was analyzed by micro GC (CP-4900, Varian).

The performance of catalytic burner was measured by varying the methanol and oxygen feed rate. The catalytic burner was simply insulated just to prevent the perturbation caused by the movement of air. The catalytic burner was located at the center of plaster box only to reduce the forced convection effect, because the characteristics of catalytic burner can be understood without perfect insulation. The flow distribution over the micro-channel and the catalyst pretreatment effect were also examined in the performance test part of silicon-based miniaturized catalytic burner.

After investigating the possibility of silicon-based catalytic burner, it was integrated with the silicon-based reformer. Then the performance of the reformer with catalytic burner was compared with the performance of the reformer with the thin film heater. Finally, the silicon-based reformer-catalytic burner stack fabrication was tried, then the performance was examined and the problems were discussed.

### 3. Results

#### 3.1. Performance of the methanol catalytic burner

In this study, two types of methanol catalytic burner were designed for performance test and stack fabrication. One had 17 parallel micro-channels and the other had 36 parallel micro-channels. The uniform gas distribution is important in micro-channels, because the temperature distribution is affected by reactants distribution. Thus the distribution of reactant gas was investigated through a simulation method, before carrying out the performance test of both reactors. The gas distribution was calculated with Fluent™ at the experimental conditions of  $10 \text{ ml h}^{-1}$  reactant feed rate and 1 atm outlet pressure.

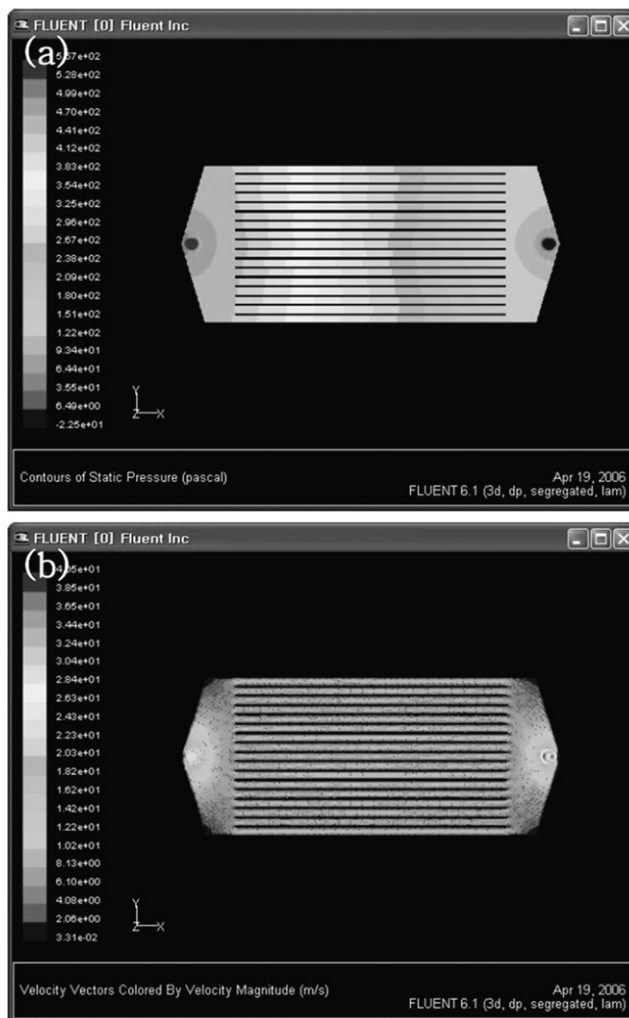


Fig. 3. Simulation with Fluent™: (a) pressure distribution over 17 parallel micro-channels; (b) velocity distribution over 17 parallel micro-channels.

The pressure distribution and the velocity distribution over 17 parallel micro-channels are shown in Fig. 3. As it can be seen in the figure, the velocity distribution is uniform through out the 17 parallel micro-channels. Thus it can be assumed that the reactants are distributed uniformly over 17 parallel micro-channels. The pressure distribution and velocity distribution over 36 parallel micro-channels are given in Fig. 4. The velocity distribution

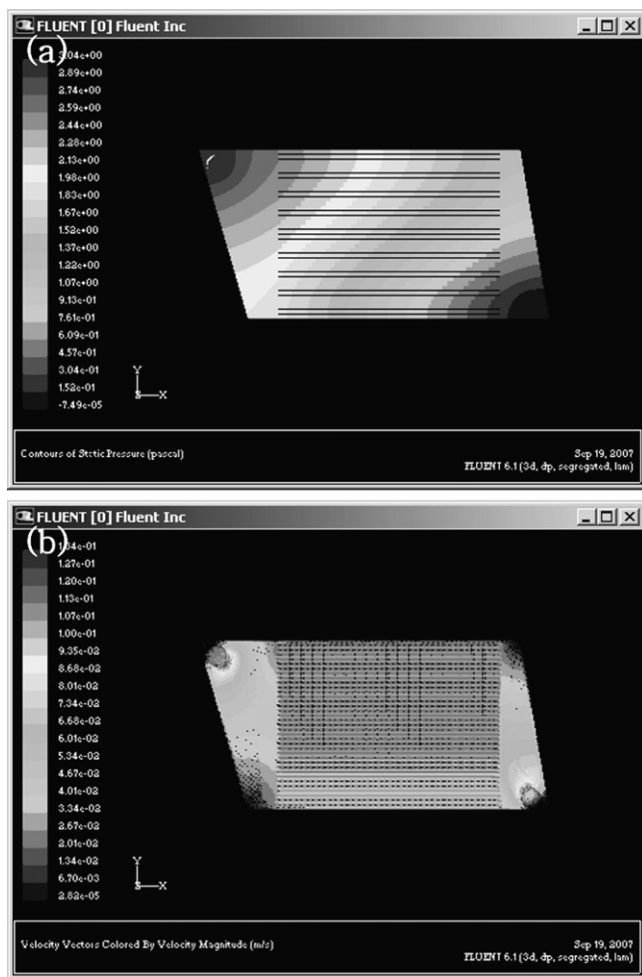


Fig. 4. Simulation with Fluent™: (a) pressure distribution over 36 parallel micro-channels and (b) velocity distribution over 36 parallel micro-channels.

over 36 parallel micro-channels is uniform over 4/5 of the channels located in a top region, however, the velocity is slower than the top region over 1/5 of the channels located in a bottom. This is due to the lower pressure at the entrance of the channels located in the bottom as it can be seen in Fig. 4(a). Nevertheless it can be said that the distribution of fluid is uniform over the 36 parallel micro-channels because the velocity is uniform over 4/5 of the channels and the velocity deviation between top and bottom is small.

The second issue of this study is to determine the catalyst pretreatment condition that may affect catalyst activity. Non-pretreatment (as-prepared), oxidation of the catalyst and reduction of the catalyst were applied as the catalyst pretreatment methods. The oxidation was carried out with  $2 \text{ ml min}^{-1} \text{ O}_2$  at  $300^\circ\text{C}$  for 3 h and the reduction was performed with  $2 \text{ ml min}^{-1} \text{ H}_2$  at  $300^\circ\text{C}$  for 3 h. In order to compare the relative characteristic of three catalysts, methanol feed rate and oxygen supply rate were fixed at  $1 \text{ ml h}^{-1}$  and  $19.9 \text{ ml min}^{-1}$ , respectively, and the amount of Pt–Al<sub>2</sub>O<sub>3</sub> catalyst loaded in the reactor was kept same as 27 mg. The temperatures of the methanol catalytic burner recorded according to the experiment time are shown in Fig. 5. As-prepared and reduced catalysts show very similar results. The conversion of 85%, the maximum temperature of  $200^\circ\text{C}$ ,

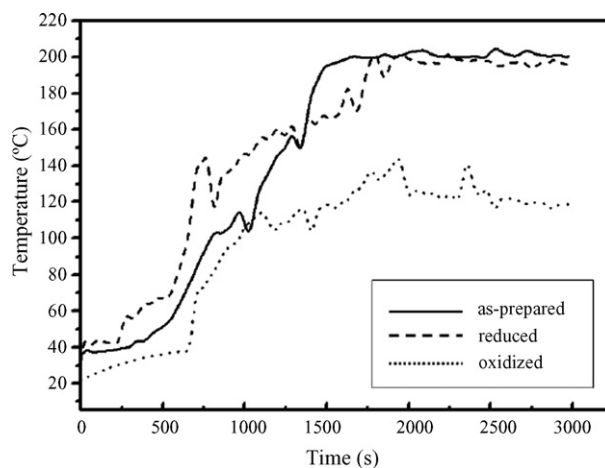


Fig. 5. The performance of the miniaturized methanol combustion burner according to catalyst pretreatment methods.

the start-up time of 1800 s and the overshooting trend were very similar. The fluctuation or overshooting of the temperature was detected at the initial stage of the start-up. This phenomenon was caused by the sudden methanol vaporization. Only some part of methanol, entering into the burner as a liquid phase, reacts with the oxygen before the temperature of the burner reaches the boiling temperature of the methanol. Last of them condense inside of micro-channel till the temperature reaches the boiling point. After passing the boiling point of the methanol, the methanol condensed inside of micro-channel suddenly vaporizes, which contributes the overshooting at the initial stage of the start-up. The oxidized catalyst showed lower performance than others. Methanol conversion was only 45% and the maximum temperature was  $130^\circ\text{C}$  at same methanol and oxygen feed rates with the as-prepared and reduced catalyst experiments. The lower performance of the oxidized catalyst is due to the PtO<sub>2</sub> that shows lower performance than Pt [15]. Considering the catalytic activity and the catalyst preparation easiness, the as-prepared catalyst was used for all following experiments.

The performance of the silicon-based miniaturized MCB was evaluated by varying the methanol feed rate to find out whether the silicon-based miniaturized MCB with micro-channel and layer type catalyst could generate sufficient heat to elevate the temperature of the reformer up to  $300^\circ\text{C}$ . The methanol feed rate was varied between  $1 \text{ ml h}^{-1}$  and  $3 \text{ ml h}^{-1}$  with an interval of  $0.5 \text{ ml h}^{-1}$ . The oxygen feed rate was controlled to maintain same oxygen to carbon ratio. The results of these experiments are shown in Fig. 6. The heat of reaction was proportional to the methanol feed rate, and the methanol conversion was kept over 90% at all methanol feed rates. The silicon-based miniaturized MCB reached the temperature of  $300^\circ\text{C}$  with the methanol feed rate of  $3 \text{ ml h}^{-1}$  showing the heat of reaction of 14 W.

### 3.2. A reformer combined with the MCB

A steam reforming of methanol reaction is an endothermic reaction, thus thermal energy should be continuously supplied to initiate and maintain the reaction. In previous paper, silicon-based miniaturized reformer with a thin film heater was

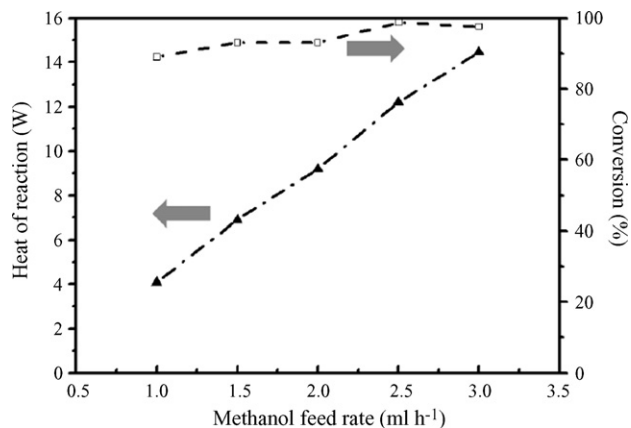


Fig. 6. Heat of reaction and conversion of the miniaturized methanol combustion burner.

developed, and it was operated successfully [5]. The silicon-based miniaturized reformer of which the temperature was tried to be controlled by the miniaturized MCB was investigated in this study. The reactions for reforming and methanol combustion were carried out at the separated micro-channels formed on different reactors.

The silicon-based miniaturized reformer was tested by using the silicon-based miniaturized MCB as an external heater source, and the performance was compared with the results of the reformer with an electric heater. The performance of the reformer with the electric heater is shown in Fig. 7. The amount of Cu–ZnO–Al<sub>2</sub>O<sub>3</sub> catalyst loaded in the reformer for this experiment was 20 mg. Methanol solution with the steam to carbon ratio of one was supplied to the reformer with the feed rate of 2 ml h<sup>-1</sup>. The relay-on-time of the temperature controller was recorded to evaluate the amount of the heat energy that was consumed to heat up the reformer and to produce hydrogen. The relay-on-time means the time of which the current flows to supply electric energy to a thin film heater.

The reformer with the electric heater needed 11 W to heat up the reformer to 320 °C and to make hydrogen, when the reformer was exposed to air with simple insulation. From the theoretical calculation, it can be known that 1.52 W should be supplied to

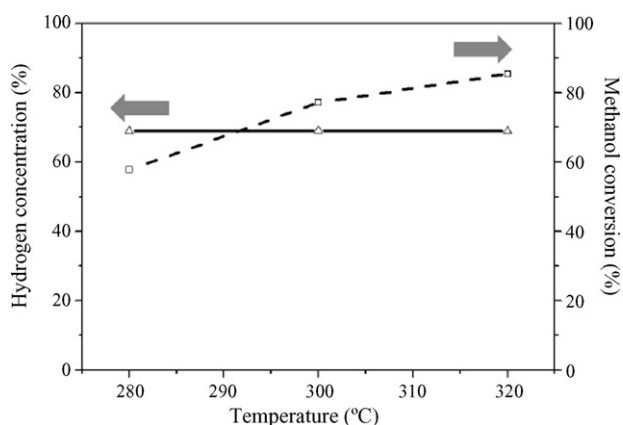


Fig. 7. The performance of the reformer of which the temperature is controlled by the electric heater.

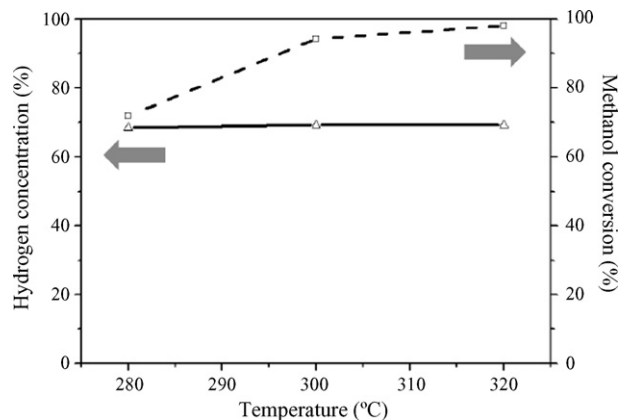


Fig. 8. The performance of the reformer of which the temperature is controlled by the methanol combustion burner.

the reformer that carry out the reforming reaction at 2 ml h<sup>-1</sup> methanol feed rate. Thus last of heat energy was discharged into air. The conversion of the methanol solution increased with the temperature, leading to the conversion of 85.4% at 320 °C.

Fig. 8 shows the performance of the reformer with the MCB. The methanol solution feed rate for the reformer was fixed at 2 ml h<sup>-1</sup>, while the temperature of MCB and methanol feed rate for MCB were varied from 280 °C to 320 °C, and 2.3 ml h<sup>-1</sup> to 3.2 ml h<sup>-1</sup>, respectively. The temperature and the heat of reaction of the MCB are shown in Fig. 9. The temperature and the heat of reaction were proportional to the methanol feed rate and finally reached 320 °C and 11.2 W with the methanol feed rate of 3.2 ml h<sup>-1</sup>. The heat energy required to make the temperature of reformer reach 320 °C was similar to that of the reformer with electric heater. Methanol conversion of the MCB was higher than 90% at all methanol feed rates. The conversion of the reformer with the MCB was higher than that of the reformer with the electric heater as shown in Figs. 7 and 8. The temperature of the reformer controlled by the electric heater showed uniform temperature distribution through out the reformer, however, the reformer with the MCB showed the temperature gradient between inlet and outlet of the reformer because of the fast methanol oxidation reaction over Pt–Al<sub>2</sub>O<sub>3</sub> catalyst at the inlet of the catalytic burner as shown in Fig. 10. Even though there was

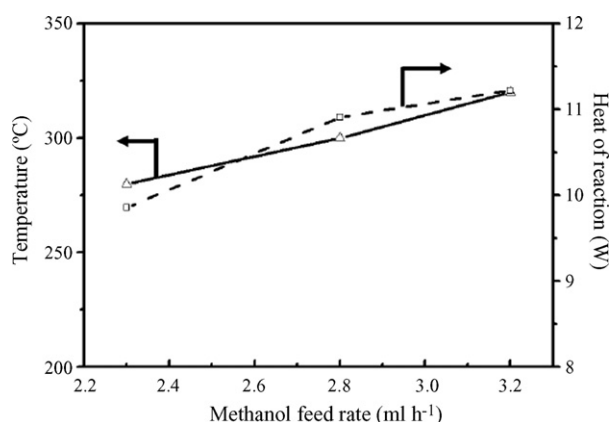


Fig. 9. Heat of reaction and temperature variation of the methanol combustion burner.

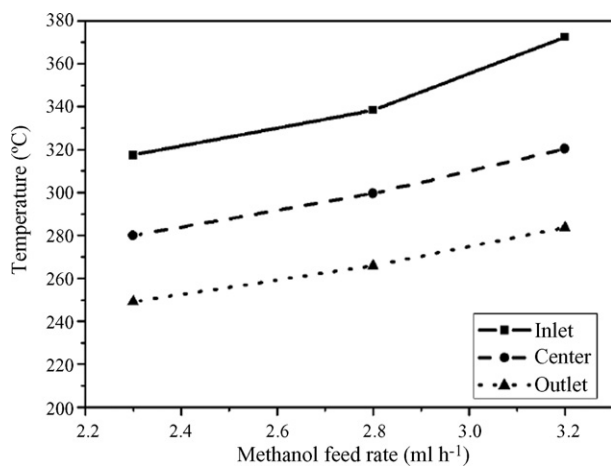


Fig. 10. The temperature distribution on the methanol combustion burner.

no big difference in temperature in vertical direction because of uniform gas distribution, temperature deviation existed in lateral direction (inlet–outlet direction). Most of methanol react at the inlet, thus cause high temperature, in other word hot spot, at the inlet. This problem can be solved by introducing fuel distributor [16]. Gas distributor solves the hot spot problem by injecting the fuel at many points of catalytic burner simultaneously. Due to the higher temperature at the inlet than the monitored temperature at the center, the reformer with the MCB showed higher conversion than that with the electric heater.

One of the expected problems of reformer-MCB system is a Pt–Al<sub>2</sub>O<sub>3</sub> catalyst degradation caused by the hot spot. Hot spot is generated due to the fast oxidation of methanol over Pt–Al<sub>2</sub>O<sub>3</sub> catalyst. To investigate the catalyst degradation phenomenon at the miniaturized catalytic burner, the durability test was performed. The durability test is useful to check the degradation of catalyst, even if it is an indirect way. The experiment was carried out over a month maintaining identical methanol and oxygen feed rate. It was turned on and off everyday except weekend. It maintained the same temperature over a month with identical methanol and oxygen feed rate showing same conversion as shown in Fig. 11. This means that the degradation of Pt–Al<sub>2</sub>O<sub>3</sub> did not occur seriously during the experiment. The

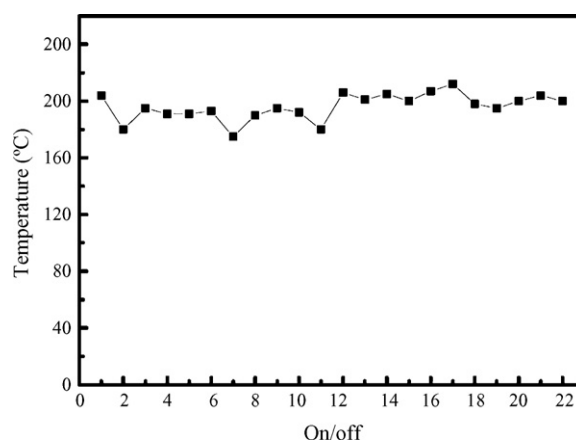


Fig. 11. Durability test of catalytic burner.

slow down of the deactivation of Pt–Al<sub>2</sub>O<sub>3</sub> catalyst in miniaturized catalytic burner may be due to the fast heat transfer through a substrate and the gas flow.

The second problem caused by high temperature at the inlet is the Cu–ZnO–Al<sub>2</sub>O<sub>3</sub> catalyst deactivation by sintering might occur. But the reforming catalyst of this experiment showed stable catalytic activity over a month even though the temperature was high. There are two deductions about this result. First is that the temperature of catalyst was different from the measured temperature. The temperature of catalyst can be lower than that of reactor surface [17]. Second is that the deactivation of catalyst originated from high temperature did not occur at the middle and at the outlet of the reactor. Even though the temperature of the reactor was high at the inlet, the temperature at the center and at the outlet of the reactor was sustainable for the Cu–ZnO–Al<sub>2</sub>O<sub>3</sub> catalyst. The most definite way to make sure this assumption is to measure the temperature of the catalyst at the surface of the catalyst layer, however it is not possible.

### 3.3. A reformer-MCB stack

Although the temperature uniformity problem remained, the miniaturized MCB showed comparable performance to the thin film heater as well as self-sustainable characteristic. In this part,

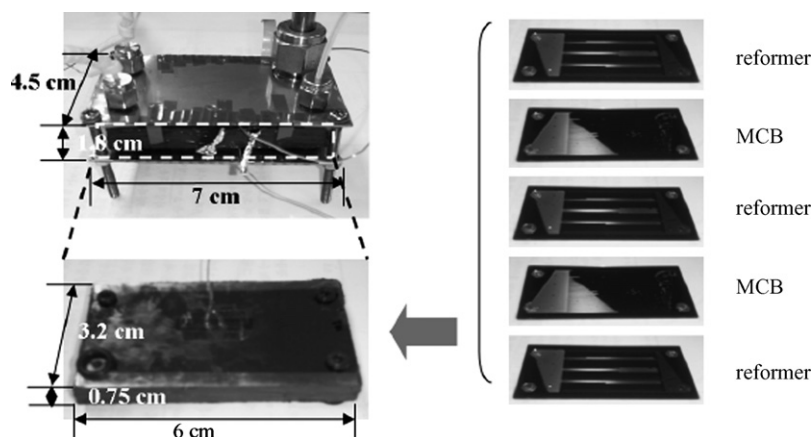


Fig. 12. The structure of the reformer-MCB stack.

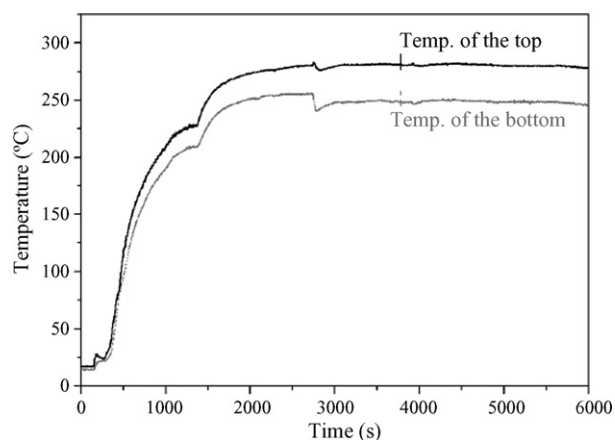


Fig. 13. The temperature of the reformer-MCB stack.

the fabrication process of a reformer-MCB stack was described and the performance of the reformer-MCB stack was discussed. The reformer-MCB stack consisted of three reformers and two MCBs. The reformer and the MCB were stacked alternately by using silicon direct bonding. Total amount of Cu–ZnO–Al<sub>2</sub>O<sub>3</sub> catalyst and Pt–Al<sub>2</sub>O<sub>3</sub> catalyst coated inside of the micro-channel were 60 mg and 54 mg, respectively. The structure of the reformer-MCB stack is shown in Fig. 12.

Methanol feed rate and oxygen feed rate for the MCB were 7 ml h<sup>-1</sup> and 140 ml min<sup>-1</sup>, respectively. Fig. 13 shows the temperature of the stack. It took 40 min to elevate the temperature from 25 °C to 280 °C through self-ignition method. Methanol conversion and heat of reaction were 90% and 30.8 W, respectively. Methanol steam reforming reaction was started by supplying methanol solution after the stack reached the target temperature. The methanol solution feed rate for reforming reaction was 8 ml h<sup>-1</sup>. Even after the endothermic reforming reaction went on, the temperature of the stack was maintained at 280 °C because the power required for evaporation and reaction of 8 ml h<sup>-1</sup> methanol was 6.1 W, 19.8% of the supplied heat by the MCB. The heat discharged through convection and radiation occupied most of the heat provided by the MCB. The reformer-MCB stack generated 120 cm<sup>3</sup> product gas showing the conversion of 65% with 8 ml h<sup>-1</sup> methanol feed rate at 280 °C. The product gas was composed of 73% hydrogen and 5000 ppm CO. Even if this result is not lower than other results, the manipulation of the stack design is necessary to increase the performance of reformer-MCB stack [18,19]. Especially, more study about the gas distribution is required to improve the performance of the reformer-MCB stack, because the performance of the stack is affected by the temperature difference between top and bottom of the stack.

#### 4. Conclusion

A methanol catalytic burner and a reformer-MCB stack were made with silicon fabrication technology and a fill-and-dry catalyst coating method. Three types of catalysts prepared in

as-prepared condition, oxidation condition and reduction condition were investigated. The as-prepared catalyst was superior to the others not only in catalyst activity but also in preparation simplicity. The methanol combustion reaction that was carried out in micro-channel of miniaturized reactor with the layer type catalyst successfully elevated the temperature of the reactor up to the target temperature by varying the methanol feed rate.

The reformer of which temperature was controlled by the silicon-based miniaturized MCB gave a better performance than the reformer with a thin film heater. Even though the temperature distribution caused by the high catalytic activity of Pt was non-uniform, the system was found to be self-sustainable. The reformer-MCB stack consisting of three reformers and two MCB was successfully fabricated and operated showing the 65% conversion. The low conversion of the stack caused by the temperature gradient between top and bottom still remains to be improved. The higher performance of the stack can be expected by improving the gas distribution of methanol in the MCB, and more efficient temperature control system of the stack can be accomplished by using the thin film heater and catalytic burner simultaneously.

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