

Chemical Vapor Deposition of Alumina Catalyst Bed in a Suspended Membrane Micro fuel Reformer

— Evaluation of the Catalyst and Demonstration of Self-sustaining

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Abstract

The micro fuel reformer with suspended membrane structure can realize good thermal isolation of the reaction area on the membrane, because heat conduction through the thin suspended membrane is quite small. However, it is difficult to form catalyst selectively on the suspended membrane. The solution can be given by the *in-situ* chemical vapor deposition (CVD) method, by which alumina is deposited from an alumina precursor selectively on the suspended membrane heated by integrated micro-heaters. The deposits were evaluated by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDX). Self-sustaining hydrogen combustion was demonstrated on the deposited alumina after platinum loading. The heated area was localized just on the membrane, and temperature difference between the membrane and the bulk substrate reached 570 K, when the temperature of the membrane was 668 °C. The maximum SV value allowable for the formed catalyst was approximately 680000 l/h.

Keywords: Micro fuel reformer, Alumina, Chemical vapor deposition, Catalyst bed, Suspended membrane

1 INTRODUCTION

Recently, increasing demand for the longer operation time of portable devices makes fuel cells attractive for portable energy sources. Among several types of fuel cell, a polymer electrolyte membrane fuel cell (PEMFC) emerges with its high energy density at low working temperature. However, the provision of hydrogen to a PEMFC remains a key issue to realize a micro-PEMFC.

One of the best devices supplying hydrogen will be a micro fuel reformer [1-3]. A micro fuel reformer reforms light hydrocarbons on site, because this allows us to utilize varieties of fuel including harmless ethanol and self-pressurized propane/butane. Using a micro fuel reformer based on micro electro mechanical system (MEMS) technology, fuel reforming for portable applications will be possible.

In the previous paper [4], we reported the method to deposit alumina catalyst beds on selective areas in a micro fuel reformer. In this paper, we report the evaluation of the alumina catalyst beds and the demonstration of self-sustaining combustion on the Pt-loaded catalyst bed.

2 CONCEPT

Varieties of hydrocarbon such as methanol, propane, butane and gasoline can be used as hydrogen sources by reforming. For portable applications, methanol is generally selected, because methanol reforming is easier than that of other hydrocarbons, and proceeds at relatively low temperature (approximately 300 °C). Also, methanol will become a standard fuel after direct methanol fuel cells (DMFCs) are commercialized for portable electronics. To

produce hydrogen from methanol, steam reforming is generally used. The total reaction of methanol steam reforming is given by



The total reaction is endothermic. Supplying heat to a reforming chamber makes the reaction go forward to produce hydrogen.

In previous study, we proposed a suspended membrane structure to realize a micro fuel reformer [5]. Figure 1 shows the conceptual structure of a micro fuel reformer with a suspended membrane. A heat source and a reforming chamber are placed at either side of the suspended membrane.

The thin membrane ensures good conductive heat transfer from the heat source to the reaction zone. By selectively patterning catalysts at the central area of the suspended membrane, this structure enables good thermal isolation of the reaction area, because the lateral heat conduction through the thin membrane is small.

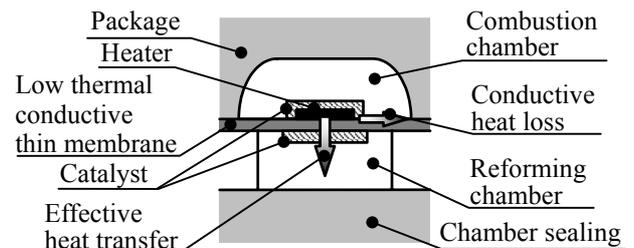


Figure 1. Conceptual structure of a micro fuel reformer with a suspended membrane

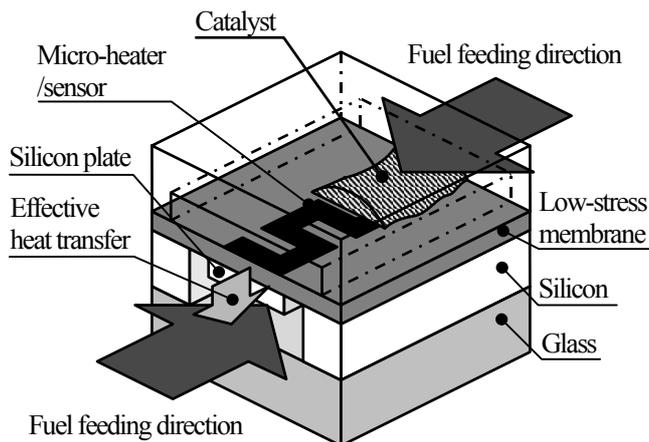


Figure 2. Structure of the micro fuel reformer

However, there was no method to form good catalyst only in the desired reaction area on the suspended membrane. Sol-gel method and wash coating are generally used to form catalyst in microreactors [6, 7]. As a result, reactions cannot be localized on the suspended membrane, resulting in considerable heat loss and by-reaction. Screen-printing was used to form catalyst on limited areas [8, 9], but mechanical stress by screen-printing easily broke the mechanically-weak suspended membrane.

To solve these problems, we have developed the *in-situ* CVD method to form an alumina catalyst bed directly on the desired reaction area of the suspended-membrane microreactor. By flowing alumina precursor into the microchannel and heating the reaction areas using micro-heaters, alumina is deposited selectively on the reaction zone.

3 STRUCTURE AND FABRICATION

Figure 2 shows the structure of the prototyped micro fuel reformer with the suspended membrane. The upper and lower sides of the suspended membrane are used for fuel reforming and catalytic combustion, respectively. The suspended membrane is composed of a low-stressed SiO₂ membrane and a silicon center plate. Micro-heaters and thermometers made of Pt/Ti are formed on the SiO₂ membrane. The SiO₂ membrane with low thermal conductivity decreases heat conduction from the central area of the membrane to an outer frame. The silicon plate with high thermal conductivity prevents hot spots, which can break the micro-heaters. The microchannels are covered with Pyrex glass substrates where inlets and outlets are opened.

The fabricated device [5] is subjected to alumina deposition test, which is described in the next section. After depositing alumina catalyst bed on the suspended membrane, tetraamine platinum (II) chloride ([Pt(NH₃)₄]Cl₂) solution is flowed into the microchannel on the combustor side. In order to evaluate the catalyst, self-sustaining hydrogen combustion was demonstrated.

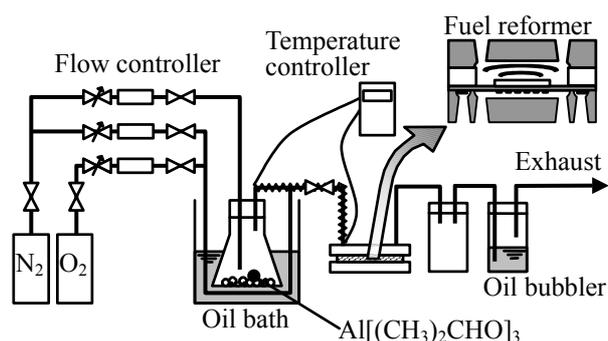
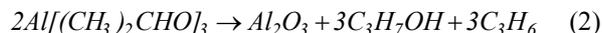


Figure 3. Diagram of the *in-situ* alumina CVD system

4 EXPERIMENTAL

4.1 Alumina Deposition

Figure 3 is the diagram of the *in-situ* alumina CVD system. Aluminum tri-isopropoxide (Al[(CH₃)₂CHO]₃) is vaporized using an oil bath, and fed to the lower microchannel of the microreactor with nitrogen carrier gas [10]. The microreactor is set on a stainless holder with sealing sheets. The oil bath, the microreactor and stainless tubes are maintained at 160 °C using a NiCr wire heater. The micro-heaters formed on the suspended membrane are heated up to 300 °C by feed-back controlling the temperature. After oxygen is fed to a microreactor, alumina CVD reaction starts on the area heated by the micro-heaters. In stoichiometry, the CVD reaction is given by



The reactant gas is exhausted through an oil trap and an oil bubbler.

Table 1 shows tested CVD conditions. From the condition (b) to the condition (a), the temperature of the oil bath changes to 190 °C from 160 °C. The temperature of the micro-heaters was kept at 300 °C on both conditions. On condition (a) and (b), 1.69 W (85.2 V, 19.8 mA) and 0.25 W (35.7 V, 7.0 mA) was consumed by the micro-heaters in steady state, respectively.

Table 1. CVD conditions

		(a)	(b)
Flow rate	N ₂ to the source vaporizer	37 ml/min	16 ml/min
	N ₂ to the microreformer	99 ml/min	120 ml/min
	O ₂ to the microreformer	157 ml/min	121 ml/min
Temperature of the oil bath		160 °C	190 °C
Deposition time		10 min	10 min

4.2. Evaluation of Deposited Alumina

After deposition, the microchannel was observed using a scanning electron microscope. Figures 4 and 5 show observed points in the microchannel for condition (a) and (b), respectively. Figures 6 and 7 show the scanning electron micrographs (SEMs) of the deposit. On the condition (a), the

deposition occurred almost on the suspended membrane as shown in Figure 6, and the deposit is roughly spherical. The deposit on silicon plate was almost stripped off after 6 days from the deposition. It can be thought that the deposit contained partly-reacted precursor and/or by-products, which decomposed by humidity.

On the condition (b), the deposit on the suspended membrane is smooth as shown in Figure 7. In this case, the deposits were not stripped off. This indicates that the CVD reaction was improved on the condition (b). The reason is that alumina precursor can easily decompose to alumina by making the temperature of the oil bath into 190 °C. However, the surface area is smaller than the porous deposits.

The atomic composition of the deposits was analyzed by energy dispersive spectroscopy (EDX). Table 2 shows the EDX results. The deposit on the condition (a) is mainly composed of Al and O, but contained C at 6 atom % to prove alumina-like. This supports the above assumption that by-products and the fragments of the alumina precursor were also deposited on the condition (a). On the other hand, the deposit on the condition (b) is only composed Al and O. However, these deposits are not close to stoichiometric alumina (Al₂O₃). This is partly because the atomic composition measured by EDX is not quantitatively correct.

Table 2. EDX results of the deposits

		Atom (%)				
		C	O	Al	Si	Total
Condition	(a)	6	61	19	13	100
	(b)	0	87	13	0	100

4.3 Demonstration of Localized Catalytic Combustion

By using [Pt(NH₃)₄]Cl₂ solution as the impregnation solution, platinum catalyst is loaded on the deposit alumina in the condition (b). Then, hydrogen combustion was demonstrated using a setup shown in Figure 8. The fuel reformer was held by the stainless tube, and hydrogen and air were fed to the microchannel. The flow rate of hydrogen and oxygen was 10 sccm and 40 sccm, respectively. The micro-heaters formed on the suspended membrane were heated up to 150 °C for ignition. The temperature of the combustion was measured by using the infrared camera.

We calibrated the emissivity of the sample for the infrared camera according to the following method. The silicon coated black spray was heated using a hotplate, and the surface temperature of the fuel reformer was measured using the infrared camera. We selected the emissivity when the temperature measured using the infrared camera was nearly equal the temperature measured using the hotplate.

Figure 9 shows the thermograph of the combustion test, and Figure 10 shows the temperature profile on the line in Figure 9. The heated area was localized just on the membrane, and temperature difference between the membrane and the bulk substrate reached 570 K, when the temperature of the membrane was 668 °C. Combustion was maintained in the microchannel (1 mm in width, 0.3 mm in depth) whose size is below the quenching length of hydrogen (0.6 mm).

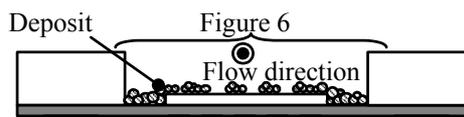


Figure 4. Observed points in the microchannel for condition (a)

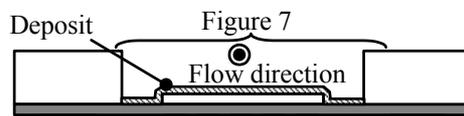


Figure 5. Observed points in the microchannel for condition (b)

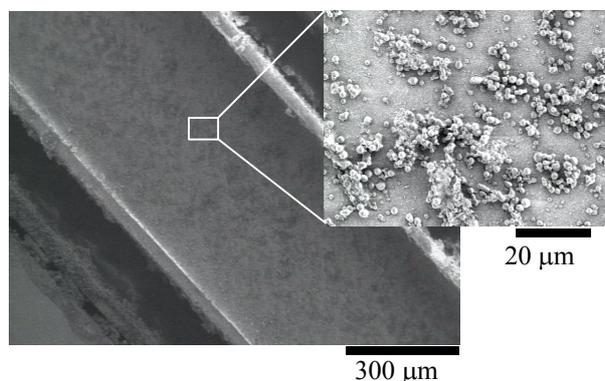


Figure 6. SEM of the deposit inside the microchannel for the condition (a)

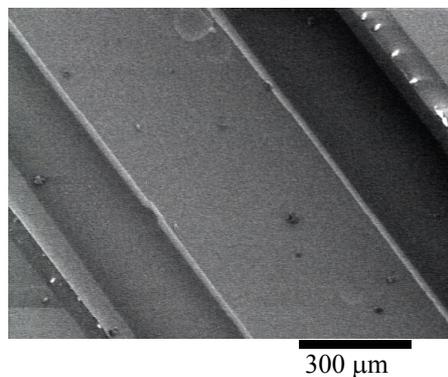


Figure 7. SEM of the deposit on the microchannel for the condition (b)

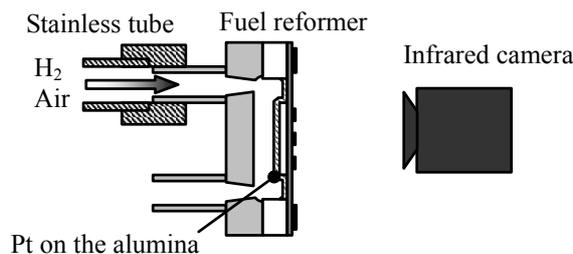


Figure 8. Setup for the combustion test

Figure 11 shows the relationship between the flow rate of hydrogen and the maximum surface temperature on the fuel reformer, to which air was constantly supplied at 40 sccm. The maximum temperature rose from 647 °C to 668 °C, when the hydrogen flow rate increased from 7 sccm to 10 sccm, and saturated at larger hydrogen flow rate. The stoichiometric flow rate of hydrogen is 16 sccm. This result indicates that the capacity of the catalyst was used up around a hydrogen flow rate of 10 sccm. This flow rate corresponds to a SV (space velocity) value of about 680000 1/h.

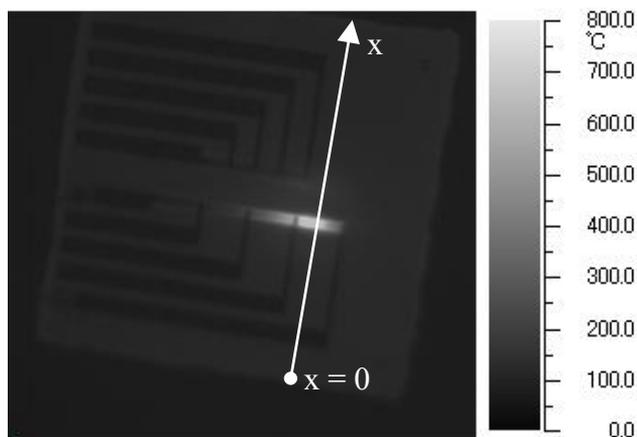


Figure 9. Thermograph of the micro fuel reformer during the combustion test

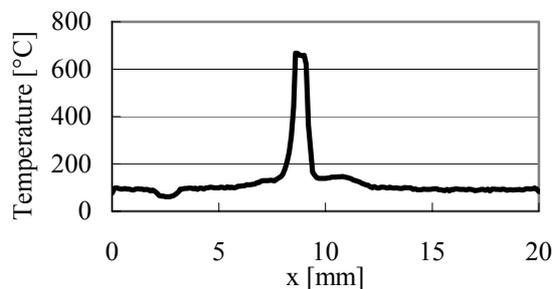


Figure 10. Temperature profile on the line in Figure 9

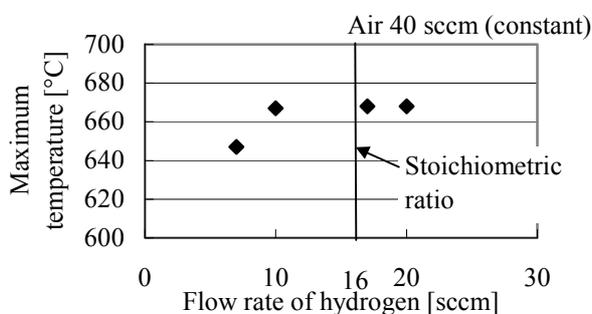


Figure 11. The relationship between hydrogen flow rate and the maximum temperature

5 CONCLUSION

To selectively form catalyst in suspended membrane microreactors, we studied the *in-situ* CVD of alumina catalyst bed, by which alumina is deposited from alumina precursor ($\text{Al}[(\text{CH}_3)_2\text{CHO}]_3$) selectively on the suspended membrane heated by integrated micro-heaters. The deposition occurred selectively on the suspended membrane. The deposits were observed by SEM and analyzed by EDX. Nano or micrograined deposit with larger surface area was obtained when the temperature of the precursor was low (160 °C). However, it was not stable, because it contained by-product and/or the fragments of the precursor as confirmed by EDX. At a higher precursor temperature (190 °C), the stable deposit without carbon was obtained, but the deposit was a smooth thin film with smaller surface area.

Pt was loaded on the deposited alumina, and self-sustaining hydrogen combustion was demonstrated on the catalyst. The membrane was locally heated by combustion up to 668 °C, and temperature difference between the membrane and the bulk substrate reached 570 K. The maximum SV value allowable for the formed catalyst was approximately 680000 1/h. This microreformer achieves excellent heat isolation, which suggest to the possibility of high total efficiency in fuel reforming.

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