

Chemical Vapor Deposition of Alumina for Catalyst Bed in a Suspended Membrane Microreformer

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Abstract

This paper describes *in-situ* chemical vapor deposition (CVD) method to deposit alumina catalyst bed selectively on the suspended membrane of a microreactor. The microreactor 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* CVD method, by which alumina is deposited from alumina precursor selectively on the suspended membrane heated by integrated micro-heaters. Suspended-membrane microreactors were fabricated, and an *in-situ* CVD system using aluminum tri-isopropoxide ($\text{Al}[(\text{CH}_3)_2\text{CHO}]_3$) as the precursor was set up. In the first trial, CVD-product was selectively deposited on the suspended membrane, as intended. The CVD-product was composed of particles with a diameter of about 2 μm . The energy dispersive spectroscopy (EDX) found that the CVD-product was mainly composed of Al and O, but contained C at less than 10 atom %. The CVD-product is alumina-like, but includes by-products and the fragments of the precursor.

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

1 INTRODUCTION

Recently, increasing demand for the longer operation time of portable information 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. There are several options for providing hydrogen, such as reforming hydrocarbons, storing hydrogen in metal hydride, high-pressure containers and carbon nanostructures (nanotubes, nanofibers), and producing hydrogen from the alkaline solution of sodium borohydride (NaBH_4).

One of the best choices will be reforming light hydrocarbons portably, because this allows us to utilize varieties of fuel including harmless ethanol and self-pressurized propane/butane. And, using a micro-fuel reformer based on microelectromechanical system (MEMS) technology, fuel reforming for portable applications will be possible [1]. In this paper, we report the method to deposit alumina catalyst bed on selective areas in a micro-fuel reformer.

2 CONCEPT

We chose methanol as a fuel for reforming, because methanol reforming is easier than that of other hydrocarbons, and proceeds at relatively low temperature. 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 often used. The total reaction of methanol steam reforming is given by Eq. 1.



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 [2]. 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.

However, there was no method to form good catalyst only on the desired reaction area. Sol-gel method and wash coating are generally used to form catalyst in microreactors, but the catalyst covers the overall wall of the microchannel. As a result, reactions cannot be localized on the suspended membrane, resulting in considerable heat loss and by-reaction. Screen-printing is used to form catalyst on limited areas, but mechanical stress by screen-printing easily breaks the mechanically-weak suspended membrane. To solve these problems, we have developed *in-situ* CVD method to form alumina catalyst beds 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.

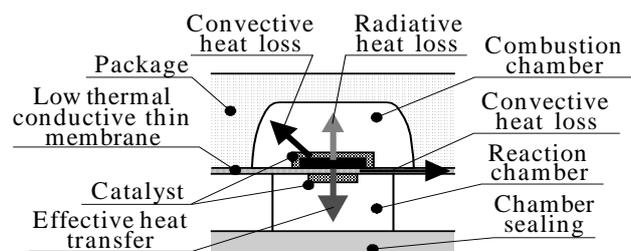


Figure 1. Conceptual structure of a micro-fuel reformer with a suspended membrane

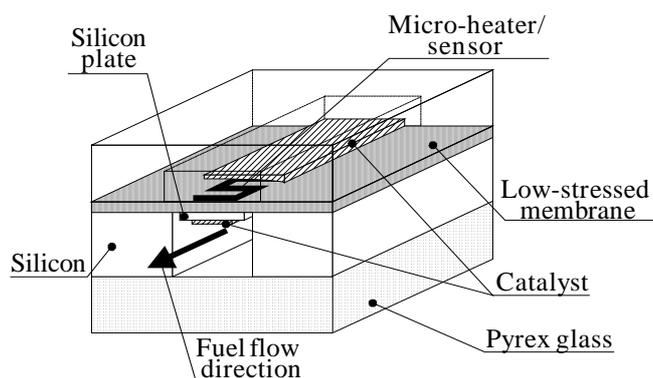


Figure 2. Structure of the micro-fuel reformer

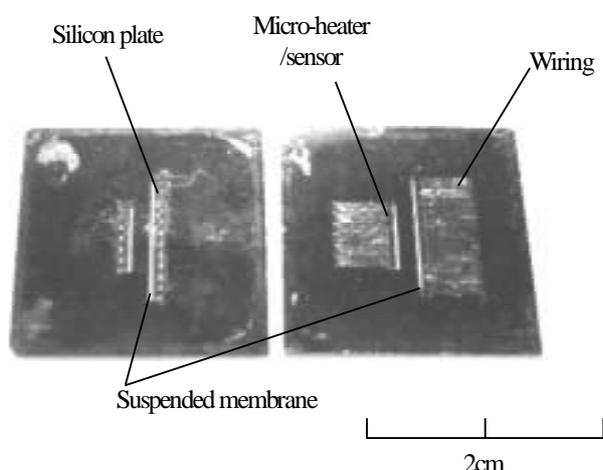


Figure 3. Microreactor with the suspended membrane structure

3 STRUCTURE AND FABRICATION

Figure 2 shows the structure of the prototyped micro-fuel reformer with the suspended membrane. The upper and lower side of the suspended membrane are used for fuel reforming and catalytic combustion, respectively. The suspended membrane is composed of a low-stressed SiO_2 membrane and a silicon center plate. Micro-heaters and thermometers made of Pt/Ti are formed on the SiO_2 membrane. The SiO_2 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 fabrication process of the micro-fuel reformer is detailed in Ref. [2]. A $4 \mu\text{m}$ thick SiO_2 film is formed by a home-made low stress plasma enhanced CVD system using tetraethoxysilane (TEOS) as a source gas. The micro-heaters, thermometers and their electrical connectors are formed on the SiO_2 film by electron beam evaporation with two lift-off processes. Then, 1 mm wide, 10 mm long microchannels are etched from the back side by deep reactive ion etching (DRIE). Figure 3 shows the fabricated device.

The fabricated device is subjected to alumina deposition test, which is described in the next section. After depositing alumina catalyst bed

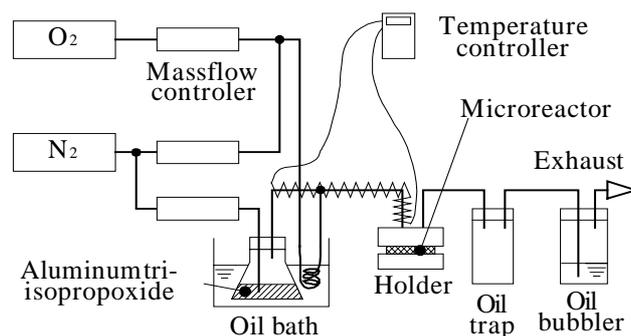


Figure 4. Diagram of the *in-suit* alumina CVD system

Table 1. CVD condition

Feeding rate	N_2 to the $\text{Al}[(\text{CH}_3)_2\text{CHO}]_3$ vaporizer	36.8 ml/min
	N_2 to the microreactor	99.2 ml/min
	O_2 to the microreactor	156.9 ml/min
Temperature of the micro-heaters		300 °C

on the suspended membrane, tetraammine platinum (II) chloride ($[\text{Pt}(\text{NH}_3)_4]\text{Cl}_2$) solution is flowed into the microchannel on the combustor side, and then reduced by flowing hydrogen and heating the micro-heaters to load platinum on the catalyst bed. The platinum loading on the deposited catalyst bed and the evaluation of the catalyst will be included in future works.

4 EXPERIMENTAL

4.1 Experimental Setup

Figure 4 shows the diagram of the *in-suit* alumina CVD system. Aluminum tri-isopropoxide ($\text{Al}[(\text{CH}_3)_2\text{CHO}]_3$) is vaporized using an oil bath, and fed to the lower microchannel of the microreactor with nitrogen carrier gas [3]. The microreactor is set on a stainless holder with sealing sheets. The oil bath, the microreactor and stainless tubes are maintained at 125 °C using a NiCr line 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, the CVD reaction starts on the area heated by the micro-heaters. The reactant gas is exhausted through an oil trap and an oil bubbler.

4.2 Result and Discussion

Table 1 shows CVD condition. In the first trial, deposition was performed in 10 min. Nitrogen was fed to the vaporizer of alumina tri-isopropoxide at 36.8 ml/min, and directly to the microreactor at 99.2 ml/min. Oxygen was fed to the microreactor at 156.9 ml/min. The integrated micro-heaters were heated at 300 °C, and at this time, 1.69 W (85.2 V, 19.8 mA) was consumed by the micro-heaters in steady state.

After the deposition, the microchannel was observed using an optical microscope and a scanning electron microscope. Overall, CVD-product was deposited mostly on the suspended membrane, and little CVD-product was observed on the glass side. Selective CVD on the suspended membrane was basically demonstrated.

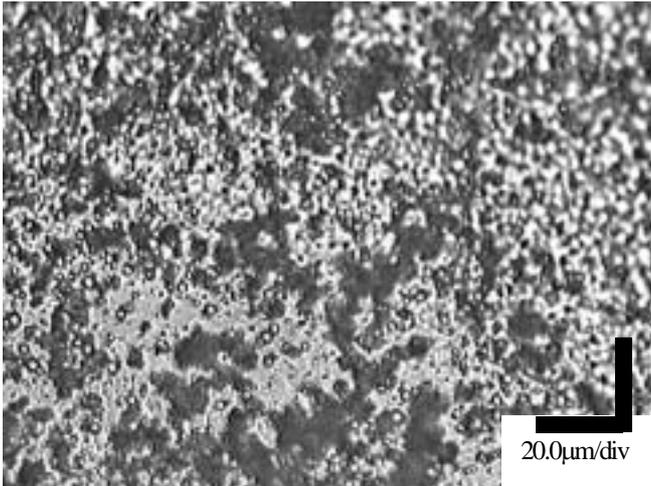


Figure 5. Optical micrograph of the CVD-product on the silicon plate

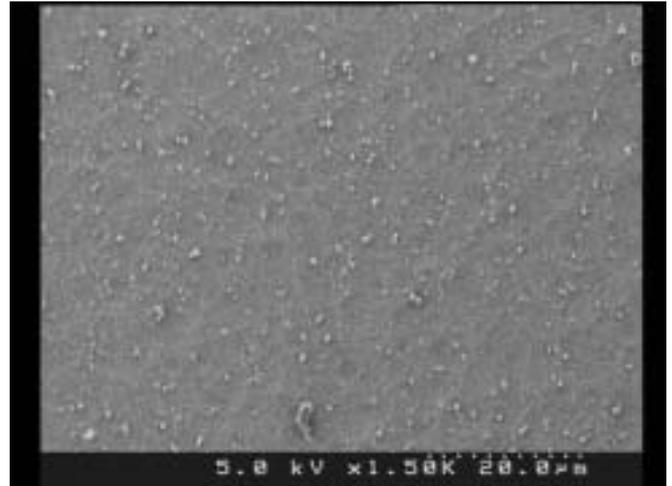


Figure 7. SEM of the CVD-product on the silicon plate

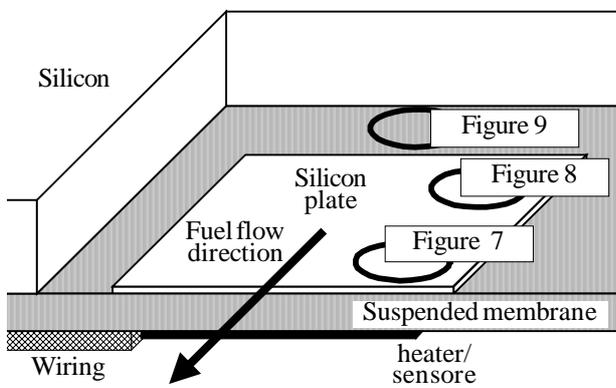


Figure 6. Observed points in the microreactor

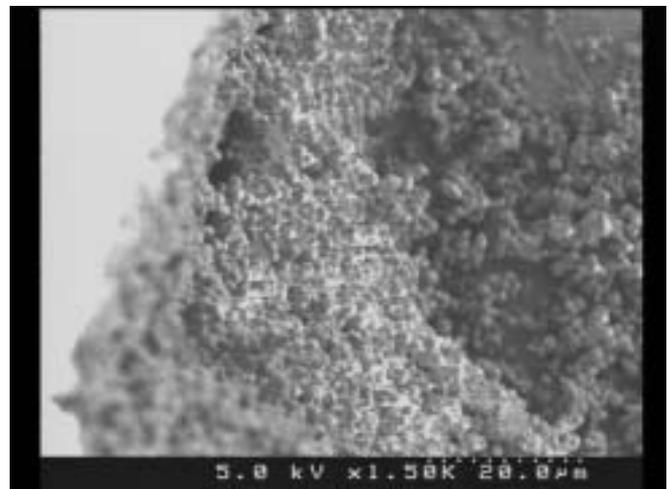


Figure 8. SEM of the CVD product on the SiO₂ membrane near the inlet

Figure 5 shows the optical micrograph of the CVD-product on the silicon plate. Observed points in the microchannel are indicated in Fig. 6. The CVD product consists of many fine particles. Figures 7-9 show the scanning electron micrographs (SEMs) of the CVD product. Figure 7 was taken on the silicon plate after 6 days from the deposition. Particles shown in Fig. 5 were almost stripped off, and a deposited film under the particles was observed. As shown in Fig. 8, the CVD product was thickly deposited near the inlet. On the SiO₂ membrane inside the microchannel, similar CVD products were deposited. From these figures, the particles are found to be roughly spherical and 2 μm in diameter.

The atomic composition of the CVD product was analyzed by energy dispersive spectroscopy (EDX). Table 2 shows the EDX result. The CVD product was mainly composed of Al and O to prove alumina-like. However, the CVD product is not close to stoichiometric alumina (Al₂O₃), and contains C. By-products and the fragments of the alumina precursor were also deposited. From this result, by annealing with oxygen purging, some unstable CVD-products will react and vaporize, and better alumina with a lot of pores and/or microcracks, which are preferable for large surface area, is expected to be obtain. On the condition shown in Table 1, many particles were deposited, and the CVD-product included by-products and the fragments of the alumina precursor. From this result, it is found that the flow rate of the source gas is too high on this condition. In future works, we will try

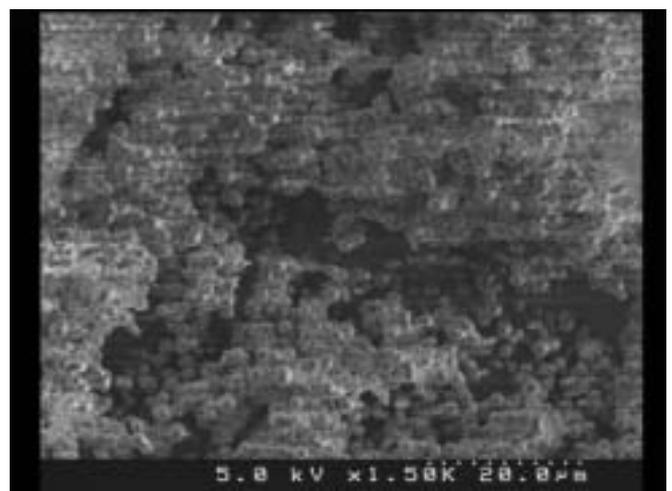


Figure 9. SEM of the CVD product on the SiO₂ membrane inside the microchannel

Table 2. EDX result of the CVD-product

Atom(%)	C	O	Al	Si	Total
On Si plate	6.44	60.92	19.24	13.40	100.00
On SiO ₂ membrane	9.82	64.31	25.45	0.41	100.00

other deposition conditions. Not only the concentration of the source gas, but also the residence time of the gas, the temperature of the membrane and its distribution are parameters to be optimized. Also, the structural analysis of deposited alumina by x-ray diffraction (XRD) is included in future works, because β -alumina is known to have better catalysis.

5 CONCLUSION

Our micro-fuel reformer has a suspended membrane, on either side of which reforming reaction or catalytic combustion proceeds. To realize good thermal isolation of the reaction area by the suspended membrane structure, catalyst must be formed selectively on the suspended membrane. For this requirement, we proposed the *in-situ* CVD of alumina catalyst bed, by which alumina is deposited from alumina precursor selectively on the suspended membrane heated by integrated micro-heaters.

We fabricated suspended-membrane microreactors and set up an in-situ CVD system using aluminum tri-isopropoxide ($\text{Al}[(\text{CH}_3)_2\text{CHO}]_3$) as the precursor. As the first trial, deposition was performed at 300 °C in 10 min. CVD-product was deposited selectively on the suspended membrane, as intended. The CVD-product was composed of particles with a diameter of about 2 μm . The adhesion of the particles was poor, and some of the particles were stripped off in 6 days from the deposition. The energy dispersive spectroscopy (EDX) found that the CVD-product was mainly composed of Al and O, but contained C at less than 10 atom %. The CVD-product is alumina-like, but includes by-products and the fragments of the precursor.

Future works include to find better deposition conditions and to analyze the structure of deposited alumina by x-ray diffraction (XRD).

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