

## Development of Micro Catalytic Combustor with Pt/Al<sub>2</sub>O<sub>3</sub> Thin Films

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Micro catalytic combustion of butane in microtube is investigated. Porous alumina fabricated on the inner surface of microtube through anodic oxidation of Al is employed for the support of Pt catalyst. Exhaust gas is sampled to measure its composition and the combustion efficiency. Combustion starts at 250 °C, and a heat release rate up to 250MW/m<sup>3</sup> is achieved in a 0.6mm ID tube. A silicon-based catalytic combustor is designed and its prototype is fabricated using MEMS technologies. The Pt/alumina catalyst layer is successfully integrated onto a silicon microchannel, and a Pyrex lid is anodically bonded onto the Si substrate. It is found in a preliminary experiment that the MEMS combustor also works well, but gives somewhat smaller reaction rate due to the thinner catalytic layer.

**Key Words:** Catalytic combustor, anodic oxidation, Pt/Al<sub>2</sub>O<sub>3</sub> catalyst, MEMS

### INTRODUCTION

Due to recent advances of mobile electronic devices such as laptop computer and cellular phone, the worldwide demand for primary and secondary batteries is growing annually and projected to be \$59 billion in 2006[1]. Li-ion battery has the highest energy density among secondary batteries for consumer use, but its energy density is projected to reach only 300Wh/kg. On the other hand, the energy density of hydrocarbon fuel such as methanol and butane is up to two orders of magnitudes larger. Therefore, local power generation having only a few percent conversion efficiency can provide much higher energy density than Li-ion batteries.

Recently, portable power generation systems of various kinds such as MEMS gas turbine[2], micro rotary IC engine[3], micro fuel cell[4], and micro thermoelectric power generator[5] are proposed and now under development. However, each system has its own challenges or drawbacks as well as advantages. Therefore, no single system is currently considered to prevail the others in real applications.

Final goal of the present study is to develop an external combustion engine such as micro steam engine or micro stirling engine[6]. In these systems, combustion in small scale is one of the most important technological issues. For

hydrocarbon fuels, reaction speed is much slower than hydrogen and quenching should occur in sub-millimeter scale. Therefore, heterogenous catalytic combustion rather than homogeneous gas phase reaction is preferred[7-11].

Sitzki et al. [7] developed so-called Swiss Roll combustors with counter flow heat exchanger lapping around the combustion region in order to reduce heat loss. They reported that onset of combustion starts at lower temperature with catalysts. Wang et al. [8] developed a micro ceramic combustor with a tape-casting method, and measured reaction rate of *n*-butane at low equivalence ratios on Pd/alumina catalysts. Arana et al. [9] fabricated suspended-tube reactor, which can significantly reduce heat loss and maintain a temperature gradient of up to 2000°C/mm. They made a catalyst layer onto the channel wall using the conventional solgel method, and found that catalytic ammonia cracking up to 1.6 W of hydrogen can be made. Spadaccini et al. [10] developed a prototype catalytic combustor for the MEMS gas turbine. They employed platinum coated form as the catalyst insert and obtained 60-70% combustion efficiency for hydrogen, but the efficiency is decreased to 10-30% for propane and ethylene near the stoichiometry condition due to its slower reaction speed. Splinter et al. [11] employed 70µm-thick porous silicon as their Pd cata-

lyst support and developed a micro membrane reactor. They showed that oxidation of CO is successfully made in their reactor.

The objectives of the present study are to develop micro catalytic combustor with anodized alumina support and to evaluate its performance in a series of laboratory experiments.

### CATALYST LAYER

In the present study, catalyst support layer is made through anodic oxidation of aluminum. The advantages of the anodized alumina support are three folds; firstly, unlike solgel methods, it is easy to control the support thickness and its characteristics such as porosity. Secondary, adhesion between alumina and aluminum is good, so that the catalyst layer is robust for thermal shock expected to occur for micro combustors. Thirdly, once aluminum layer is formed, it is easy to change it into alumina through anodic oxidation even for complex geometries.

Figure 1 shows a schematic of an anodic oxidation bath, in which 4 wt% oxalic acid solution is employed. The temperature of the solution is kept at 10 °C using an external water loop. A constant current source and stainless steel

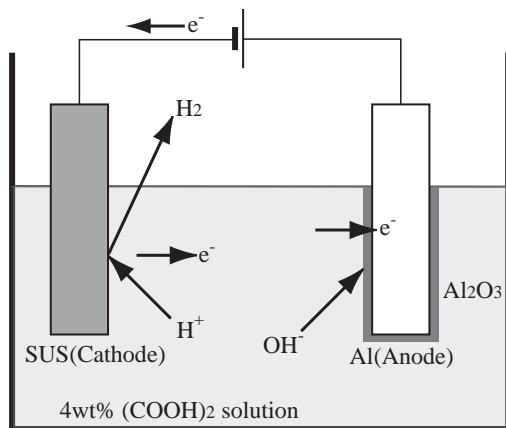


Figure 1 Schematic of anodic oxidation bath.

plate are respectively employed for the power supply and the cathode. After the oxidation followed by a bake at 350 °C for 1 hour, porous alumina ( $\gamma$   $\text{Al}_2\text{O}_3$ ) is formed on the anode surface (Fig. 2). The pore characteristics of the alumina and its thickness depend on the current density and the oxidation duration [12,13]. Then, the sample is submerged into diammine dinitro platinum (II) solution, and calcinated at 350 °C for 1 hour to make platinum impregnated into the alumina layer.

Figure 3 shows a top view of the alumina layer. Honeycomb-like pore structures can be seen, although the pore diameter and the distance between pores are not uniformly distributed. Figure 4(a) and (b) show a side view of the alumina layer anodized with current density  $I_A$  of 50A/m<sup>2</sup> and 30A/m<sup>2</sup>, respectively. Duration of the anodization is 1 hour. Thickness of the alumina is 5 $\mu\text{m}$  and 3.5 $\mu\text{m}$  respectively for  $I_A=50\text{A/m}^2$  and 30A/m<sup>2</sup>. Diameter of the pore is about 20-30nm for both cases, and in agreement with the result of Sungkono et al. [13]. When  $I_A=50\text{A/m}^2$ , distance between neighboring nanopores is about 90nm, while it is about 80nm for  $I_A=30\text{A/m}^2$ . Surface area of the alumina layer is estimated using a porous model shown in Fig. 4(c). When  $I_A=50\text{A/m}^2$ , surface area of about 2 m<sup>2</sup>/g is obtained.

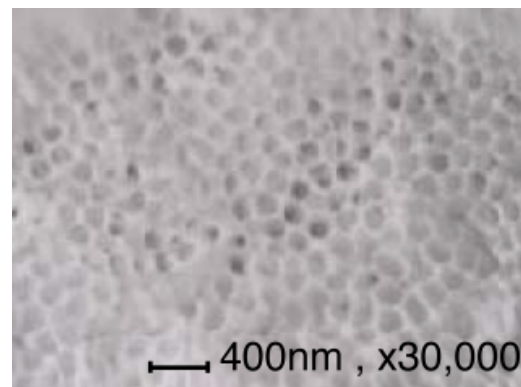


Figure 3 Top view of  $\text{Al}_2\text{O}_3$  layer fabricated with anodic oxidation at 50A/m<sup>2</sup> for 1h.

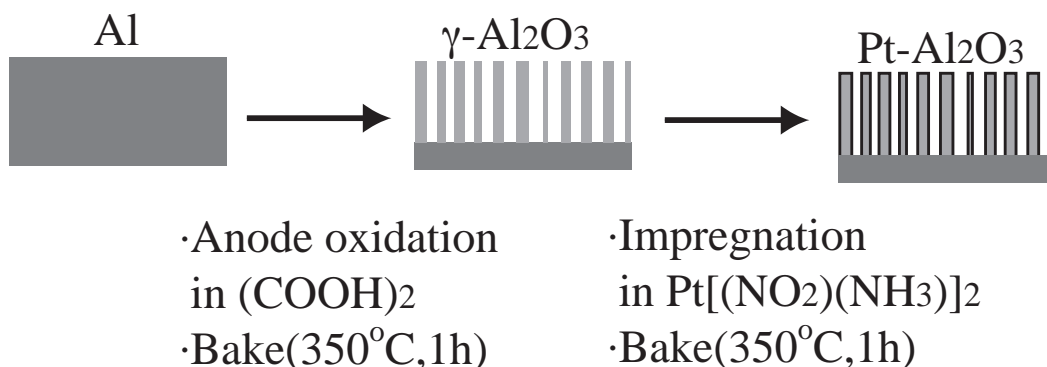


Figure 2 Fabrication process for Pt catalyst on  $\text{Al}_2\text{O}_3$  support.

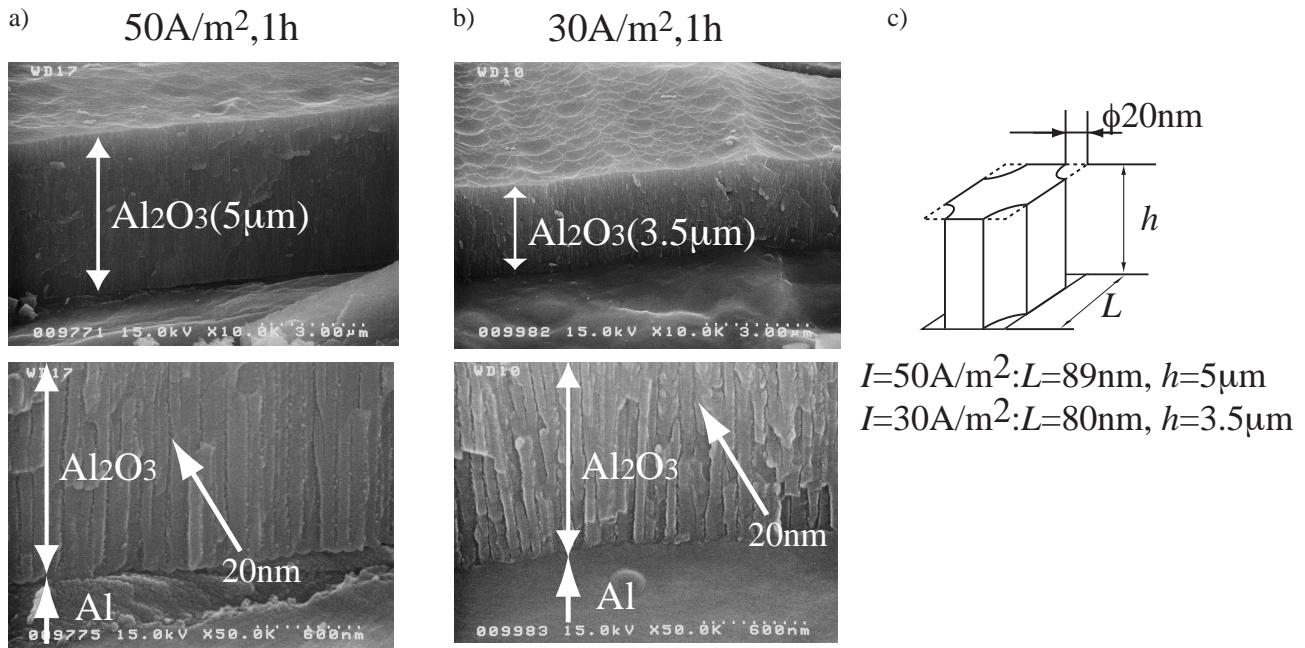
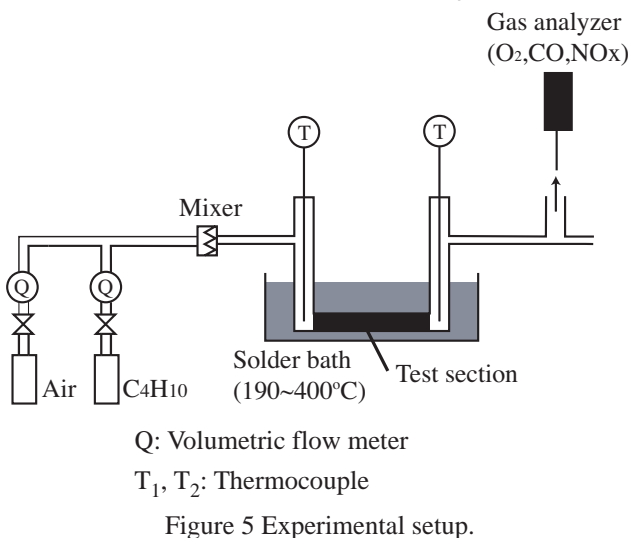


Figure 4 SEM images of  $\text{Al}_2\text{O}_3$  layer made by anodic oxidation. a), b) Side view, c) Porous model.



After impregnation of Pt, the catalyst layer is examined with X-ray fluorescent analysis in order to confirm presence of Pt. Contents of Pt in the alumina layer is designed to be around 1 wt%, although it is not directly measured in the present study.

#### COMBUSTION EXPERIMENT IN MICRO TUBE

In our first stage, catalytic layer is formed inside 0.6mm ID aluminum tube and the combustion characteristic is measured systematically. The outer diameter and the length of the tube is respectively 1mm and 50 mm.

Figure 5 shows a schematic of the present experimental setup. Air and *n*-butane are supplied from a gas cylinder through a pressure regulator and introduced into a mixer. Flow rate is separately measured using thermal mass flow

meters (Oval Corp., MASFLO). Combustion experiment is made in a solder bath, by which the solder temperature can be maintained between 190 and 400 °C. Due to high thermal conductivity and large heat capacity of solder, temperature of the combustion tube can be kept constant almost independently of the amount of heat generation at the catalyst layer. Actual temperature of the catalytic layer is estimated with the inlet and outlet gas temperature assuming that the heat transfer coefficient at the tube inner wall can be given by its theoretical value of the laminar forced convection.

Exhaust gas analyzer (TSI Inc., CA-6215) is employed to measured concentration of  $\text{O}_2$ ,  $\text{CO}_2$  and  $\text{NO}_x$ . The reaction rate is calculated using the  $\text{O}_2$  concentration at the exit. In the present experiment condition, the equivalent ratio is kept unity and the flow rate of *n*-butane is changed between 2.5 - 25 sccm, which correspond to the heat generation at 100% conversion  $Q$  of 5 - 50 W. The Reynolds number is less than 20 in all the experimental condition examined. Therefore, velocity and thermal entrance lengths are less than the tube diameter, and their effect is believed to be minor.

Figure 6 shows reaction heat of the combustion tube anodized with  $I_A = 50\text{A/m}^2$  for 12 hours. Thickness of the alumina is estimated to be  $35\mu\text{m}$  in this anodizing condition. Onset of combustion starts around 250 °C and the heat generated is increased with the catalyst temperature. At 400 °C, 100% conversion is achieved up to  $Q=10\text{W}$ , while

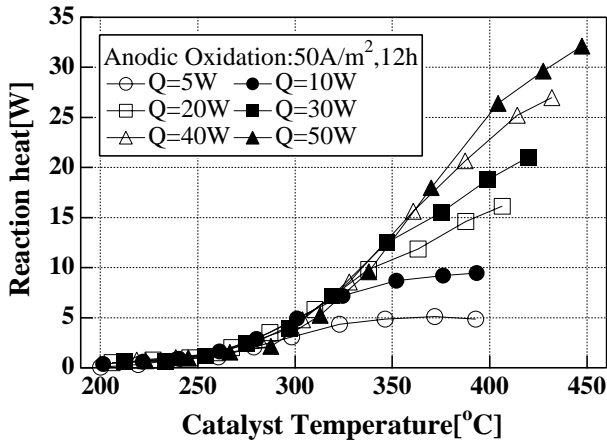


Figure 6 Reaction heat in 0.6mm ID tube with Pt/Al<sub>2</sub>O<sub>3</sub> catalyst .

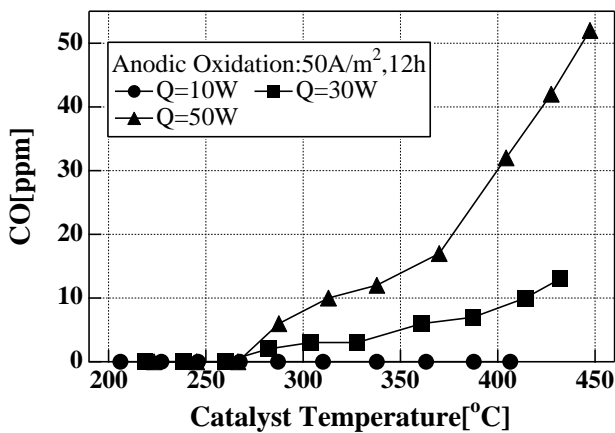


Figure 7 CO concentration in 0.6mm ID tube with Pt/Al<sub>2</sub>O<sub>3</sub> catalyst .

the maximum heat generation is 32W at 450°C for  $Q=50W$ . Therefore, heat generation density for 100% conversion is as large as 250 MW/m<sup>3</sup>, which is comparable to that of the industrial gas turbine combustors. In macro scale catalyst combustors, diffusion in the bulk fluid is the major limiting factor, and the heat generation density is generally lower than homogenous well-stirred combustors. On the other hand, in micro combustors having a small hydraulic diameter, diffusion in fluid is no more the limiting factor, and diffusion in the catalyst layer and the reaction speed itself should play a dominant role in determining the overall reaction rate.

As shown in Fig. 7, concentration of CO is almost zero for  $Q=10W$ . But, it becomes finite value when  $Q$  is larger than 10W. Note that NO<sub>x</sub> concentration is always less than 1 ppm and within the measurement accuracy of the gas analyzer.

## MEMS CATALYTIC COMBUSTOR

Figure 8 shows a schematic of Si-based catalytic combustor. Trapezoidal channels are formed into the Si substrate using anisotropic etching of (100) Si wafer. The surface area of the Pt/alumina catalytic layer is chosen as the same as that of the 0.6mm ID tube shown in the previous chapter. Hydraulic diameter of each channel is 261μm.

Fabrication process starts with patterning the SiO<sub>2</sub> layer on a Si wafer for patterning the channel and the fluid ports followed by anisotropic etching with TMAH (Fig. 9(1)). The oxide mask layer is removed with BHF and a 2nd oxide layer is formed using wet oxidation for an electrical insulation layer. Aluminum film is then evaporated and patterned in such a way that aluminum remains only inside the channel. The aluminum film is transformed into alumina using anodic oxidation as described in Chap 2. Finally, Pyrex glass wafer is anodically bonded to the Si wafer and Pt is impregnated.

Figure 10 shows a top view of the Si-based catalytic combustor having 8 parallel channels and two fluidic ports. In our preliminary experiment, polyimide tube is attached on the top of the ports using high-temperature glue. Experimental data in our first run gives somewhat smaller reaction rate if compared with the tube combustor. More detailed experiments are under development, and will be included in the final manuscript of our paper.

## CONCLUSIONS

Micro catalytic combustion of butane using a anodized alumina support is investigated. It is found in combustion experiments using 0.6mm ID tube that combustion starts at 250 °C, and a heat release rate up to 250MW/m<sup>3</sup> is achieved. A silicon-based catalytic combustor with embedded Pt/alumina catalyst layer is designed and its prototype is successfully fabricated using MEMS technologies. It is found in a preliminary experiment that the MEMS combustor also works reasonably well, but gives somewhat smaller reaction rate.

## ACKNOWLEDGMENT

This work was supported through the Grant-in-Aid for Young Scientists A (No. 14702028) by the Ministry of Education, Science, Culture and Sports (MEXT).

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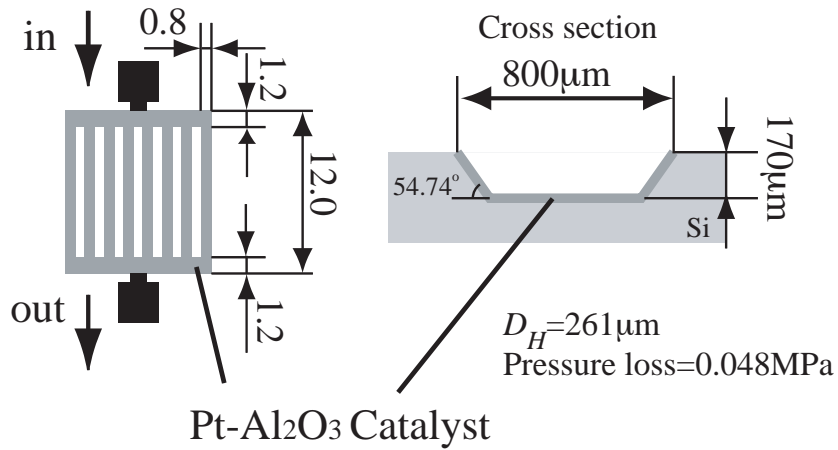


Figure 8 Schematic of micro catalytic combustor on Si substrate.

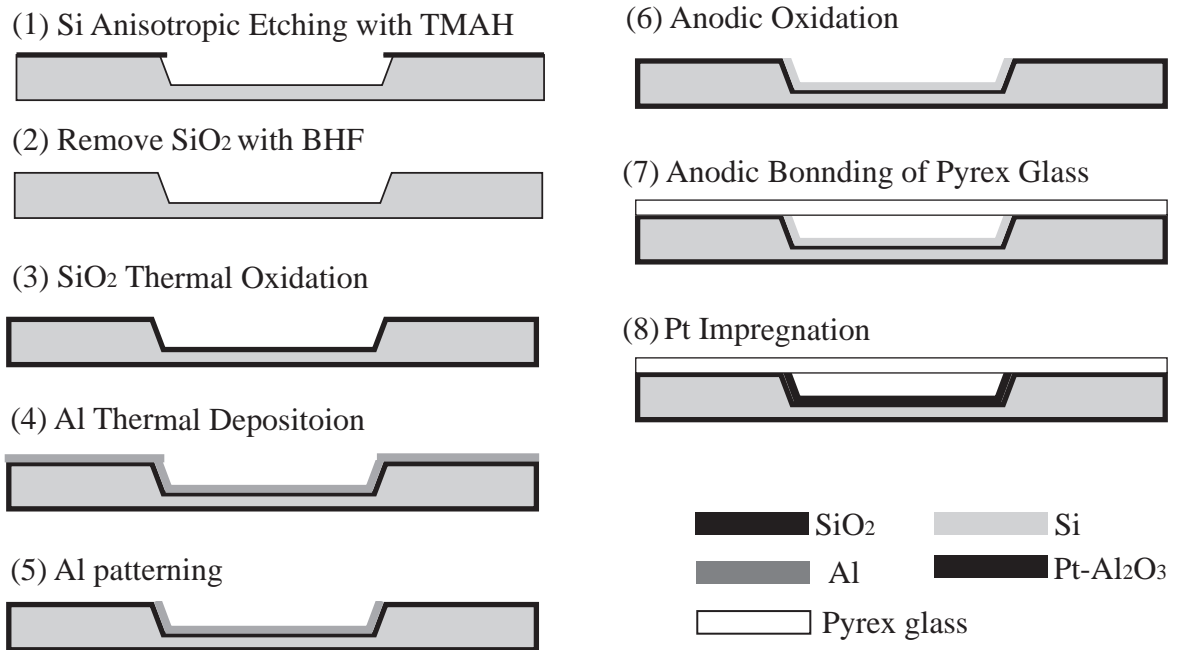


Figure 9 Process flow of Si-based micro catalytic combustor.

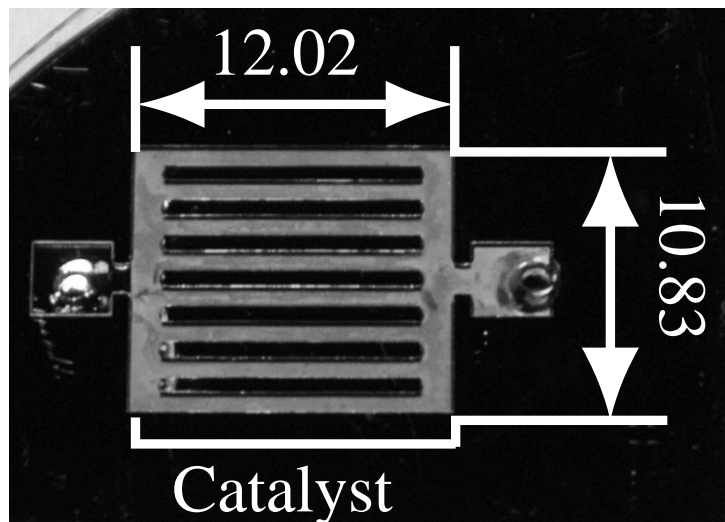


Figure 10 Photograph of Si-based micro catalytic combustor.

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