

MICRO CATALYTIC COMBUSTOR WITH TAILORED POROUS ALUMINA

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ABSTRACT

Micro-scale catalytic combustion of butane is investigated. Porous alumina fabricated through anodic oxidation of thermally-evaporated aluminum is employed for the support of Pt catalyst. A ceramic combustor with an embedded ignition heater is also designed and its prototype is fabricated using a high-precision tape-casting technology. Three-dimensional manifold, which is designed based on a series of CFD analysis, allows us to obtain an uniform velocity distribution in the combustion channel with a minimal pressure drop. The Pt/alumina catalyst layer is successfully integrated onto a ceramic microchannel. It is found in a preliminary experiment that heat release rate up to 710 MW/m^3 is achieved, whereas the reaction rate is somewhat smaller than expected from our experimental data in 0.6mm ID tube.

1. INTRODUCTION

Recently, small-scale local power generation attracts much attention for mobile electronic devices, since the energy density of hydrocarbon fuel is up to two orders of magnitudes larger than high-performance secondary batteries. Various principles such as MEMS gas turbine[1], rotary engine[2], fuel cell[3], and thermoelectric device[4] are examined, and their prototypes are under development. 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 the quenching should occur in sub-millimeter scale. Therefore, heterogenous catalytic combustion rather than homogeneous gas phase reaction is preferred. Previous studies [5-7] show that micro-scale catalytic combustion is promising. However, conventional washcoat process or sol-gel method is often employed for the catalyst layer, and sophisticated fabrication technology is used to device thermal isolation mechanisms.

Final goal of the present study is to develop cost-effective and robust combustor. For this purpose, we employed Pt/porous alumina as the catalyst and high-precision ceramic fabri-

cation technologies.

2. CATALYST LAYER

In the present study, catalyst support layer is made through anodic oxidation of aluminum film deposited on the substrate using thermal evaporation. The advantages of the anodized alumina support are three folds; firstly, unlike conventional washcoat process, 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 in micro combustors. Thirdly, once aluminum layer is formed, it is easy to change it into alumina through anodic oxidation even for

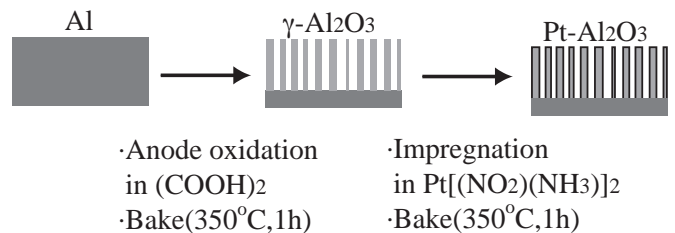


Figure 1 Fabrication process of Pt/porous alumina catalyst.

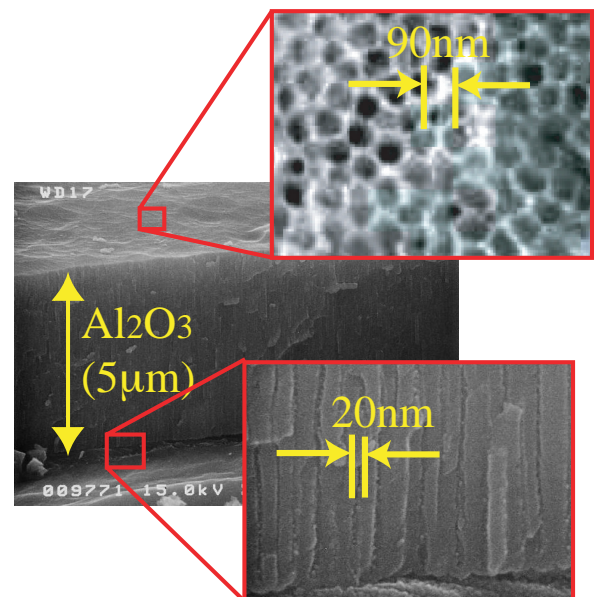


Figure 2 SEM images of porous alumina layer made by anodic oxidation at $I_A = 50 \text{ A/m}^2$.

complex geometries.

Figure 1 shows the fabrication process of Pt/porous alumina catalyst. Anodic oxidation is made using 4 wt% oxalic acid solution. The temperature of the solution is kept constant at 10 °C. A constant current source is employed for the power supply. 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. Then, the sample is submerged into diamine dinitro platinum (II) solution, and calcinated at 350 °C for 1 hour to make platinum impregnated into the alumina layer.

Figure 2 shows SEM images of the alumina layer anodized with current density I_A of 50 A/m². Honeycomb-like pore structures can be seen, although the pore diameter and the distance between pores are not uniformly distributed. The pore characteristics of the alumina and its thickness depend on the current density and the oxidation duration [8, 9]. In the present study, 5 μm -thick alumina is obtained with anodization for 50 minutes. Diameter of the pore is about 20-30 nm, which is in agreement with the result of Sungkono et al. [9]. Distance between neighboring nanopores is about 90nm, which corresponds to the surface area of 2.1 m²/g. After calcination, the surface area is markedly increased to 180 m²/g[9].

3. EXPERIMENTAL SETUP AND PRELIMINARY RESULTS

Figure 3 shows a schematic of the present experimental setup. Air and *n*-butane are supplied from a gas cylinder 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 the solder, temperature of the combustor can be kept constant almost independently of the amount of heat generation inside.

Exhaust gas analyzer (TSI Inc., CA-6215) is employed to measured concentration of O₂, CO and NOx. The reaction rate is calculated using the O₂ concentration at the exit. In the present experimental condition, the equivalent ratio is kept unity and the flow rate of *n*-butane is changed between 2.5 - 50 sccm, which correspond to the heat generation at 100% conversion Q of 5 - 100 W.

Figure 4 shows reaction heat in a 0.6 mm ID aluminum tube having 35 μm -thick anodized alumina on the inner surface. Combustion starts around 250 °C and the reaction heat is increased with the catalyst temperature. At 400 °C, 100% conversion is achieved up to $Q=10\text{W}$, while the maximum heat generation is 32 W at 450°C. Therefore, heat generation den-

sity for 100% conversion is as large as 710 MW/m³, which is comparable to that of the industrial gas turbine combustors. Concentration of CO is almost zero for $Q=10\text{W}$, while it becomes finite value when $Q>10\text{W}$.

Figure 5 shows a prototype Si-based catalytic combustor having 8 parallel channels. Hydraulic diameter of each channel is 261 μm . Trapezoidal channels formed with anisotropic wet etch have 5 μm -thick alumina on the bottom wall. Pyrex glass is anodically bonded to the Si wafer and Pt catalyst is impregnated. This early prototype gives a conversion efficiency of 55% for $Q=10\text{W}$ at 350 °C, which is somewhat smaller than estimates based on the experimental data in the 0.6 mm ID tube.

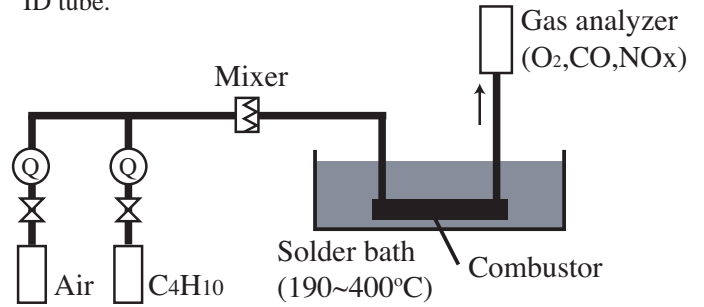


Figure 3 Experimental setup.

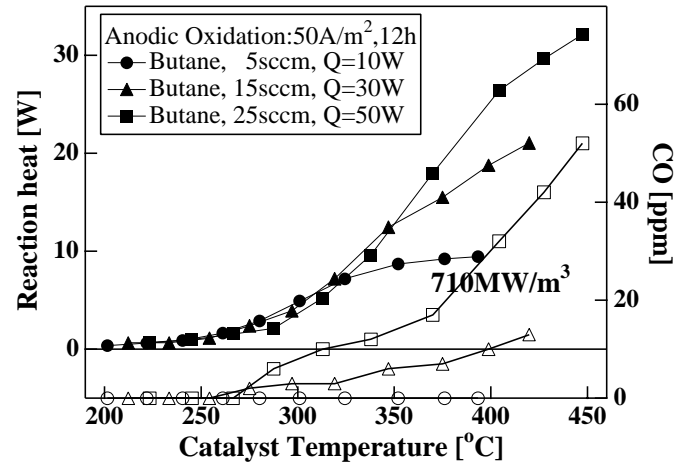


Figure 4 Reaction heat and exhaust CO concentration versus the catalyst temperature for 0.6mm ID tube combustor.

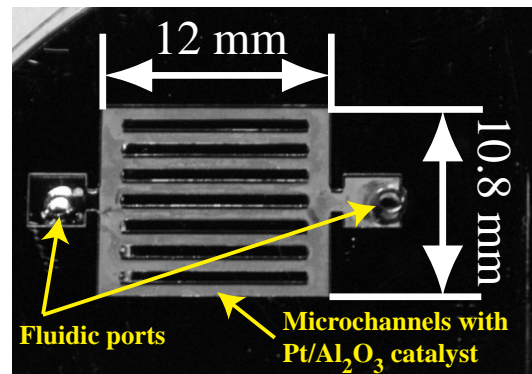


Figure 5 Si-based micro catalytic combustor.

4. CERAMIC MICRO COMBUSTOR

Our experimental data obtained in the Si-based prototype combustor demonstrate that anodized porous alumina is promising for the catalyst support in micro combustors. However, more cost-effective fabrication technology rather than Si-process is required for real applications. Another issue for the prototype is that uniform flow rate in the parallel channels is difficult when a simple manifold geometry is used. Therefore, we employ high-precision tape-casting technology developed for semiconductor ceramic packages by Kyocera Corp. Advantages are three folds; firstly, ceramic devices can be used at higher temperature than 1300 °C. Secondary, three-dimensional structures can be fabricated by stacking and firing multilayer ceramic tapes with an alignment error within 30 μ m. Thirdly, multilayer electrodes in ceramic packages are already used in industry, thus ignition heaters and anodization electrodes are easily integrated to the micro channels.

Figure 6 shows a schematic of ceramic combustor using multiple layers. The top layer is for the fluidic ports, and Fe-Ni-Co alloy tubes are soldered. The second and third layers are respectively for the manifold and the combustor channel.

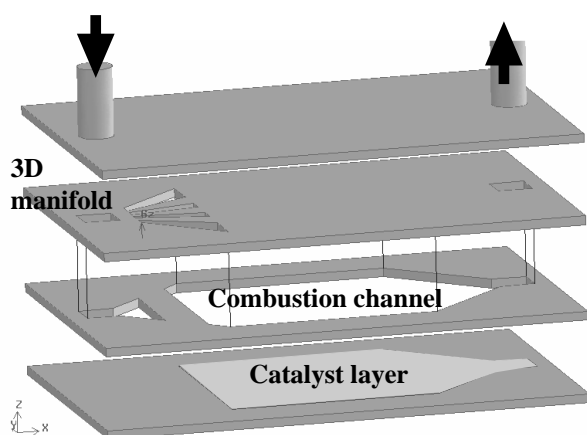


Figure 6 Schematic of ceramic micro combustor by using tape-casting technologies.

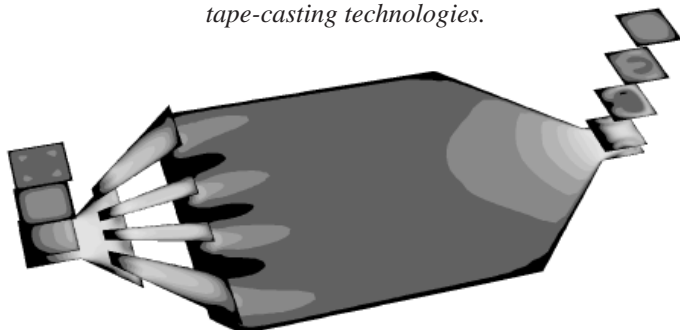


Figure 7 Contours of the velocity magnitude in the micro combustor. Velocity distributions in the center plane of the manifold and the combustion channels are shown. Total flow rate is 240 sccm. Black to white: 0-5.9 m/s.

The inlet gas firstly enters the third layer, then goes into four separate conduits in the second layer, and finally enters to the combustion channel in the third layer. The channel height is defined by the thickness of the third layer. On the top of the fourth layer, a tungsten electrode is fabricated for the electrode during the anodization. The fourth layer also has an embedded tungsten heater for ignition. Contact pads for both electrodes are located on the backside of the fourth layer. In the present design, the dimensions of the combustor is 34x20x2 mm³, and the combustor channel is 12x12x0.5 mm³.

We made a series of numerical computation with a CFD software (FLUENT 6, Fluent Inc.) in order to optimize the flow rate distribution inside the combustor channel. It is found that the flow velocity is changed by more than 20% in the cross stream direction, when a two-dimensional manifold is assumed. On the other hand, the flow velocity becomes markedly uniform by using the three-dimensional manifold shown in Fig. 6. Figure 7 shows contours of the velocity magnitude in several horizontal planes including the center plane of the channel. Because of multiple flow impingement to the manifold walls, the velocity at the center of the channel is markedly uniform within 3%. On the other hand, the pressure drop at the total flow rate of 240 sccm is as small as 67 Pa. Therefore, the 3D manifold is

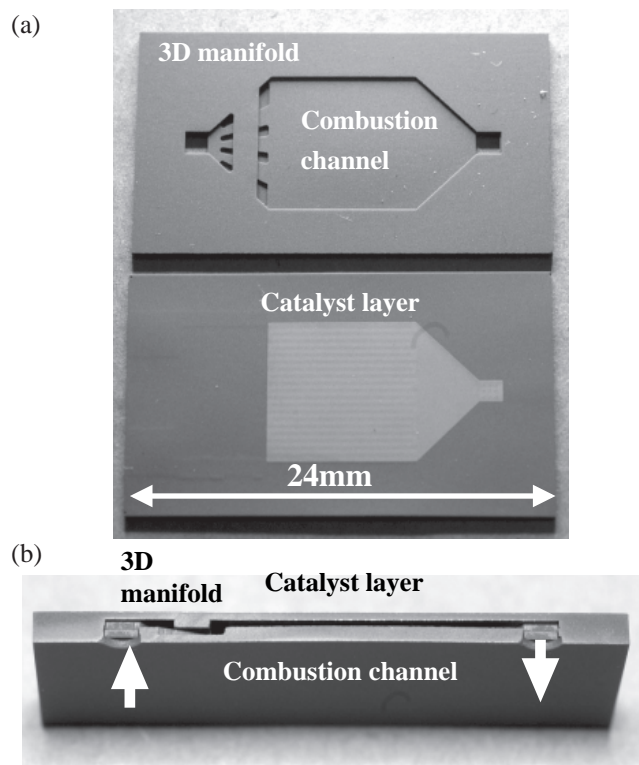


Figure 8 Ceramic micro catalytic combustor: a) Channel section (top) and catalysis plate (bottom) being assembled, b) Cutaway view along the center line.

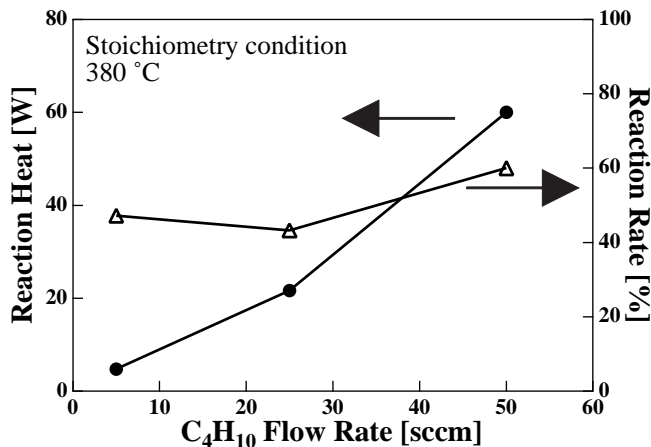


Figure 9 Reaction heat and reaction rate in the ceramic micro combustor.

suitable for uniform flow rate distribution with a minimal pressure drop.

Fabrication process starts with firing the top three layers and the fourth layer separately to make the channel section with the manifold and the catalyst plate as shown in Fig. 8(a). 20 μm -thick aluminum is thermally-evaporated onto the catalyst plate, and unwanted aluminum film outside the tungsten electrode is etched out using photolithography. Then, the aluminum layer is anodized and impregnated with Pt as described above. Finally, the channel section is bonded to the catalyst plate using low-melting glass. Figure 8(b) shows a cutaway view of the combustor.

Figure 9 shows reaction heat and reaction rate at 380 °C. Under the stoichiometry condition, the reaction heat is increased with the butane flow rate, and heat generation of 60 W is obtained at 50 sccm. On the other hand, reaction rate is lower than expected, and about 60%. It is indicated that numerical analysis including surface reaction and diffusion is necessary to optimize the design parameters of the combustor.

5. CONCLUSIONS

Pt/alumina catalyst fabricated through anodic oxidation of aluminum film is found to work well for catalytic combustion of butane. A ceramic micro combustor with an embedded ignition heater is designed and its prototype is fabricated using a high-precision tape-casting technology. Three-dimensional manifold allows us to obtain an uniform velocity distribution in the combustion channel with a minimal pressure drop. The catalyst layer is successfully integrated onto the ceramic microchannel. It is found in a preliminary experiment that heat release rate up to 710MW/m³ is achieved, whereas the reaction rate is somewhat smaller than expected from our experi-

mental data in a small-diameter tube.

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