Development of Micro Catalytic Combustor Using Ceramic Tape Casting

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Abstract

Micro-scale catalytic combustor fueled by butane is investigated. A cost-effective ceramic combustor is developed using high-precision tape-casting technology. Nano-porous alumina fabricated through anodic oxidation of aluminum layer is employed for the support of Pd catalyst. It is found in a preliminary experiment that complete fuel conversion corresponding to 58 MW/m^3 heat generation is achieved at 400 $^{\circ}$C for n-butane fuel. Catalytic combustion on the Pd/nano-porous alumina is modeled with the aid of a 1-D plug flow model. CFD analysis is also made to predict performance of the combustor at higher temperatures.

Key Words: Catalytic Combustion, Pd/nano-porous Alumina, Ceramic Combustor, Anodic Oxidation, Microchannel

1. Introduction

Due to recent advances of mobile electronic devices and autonomous robots, the worldwide demand for secondary batteries is growing rapidly. Although Li-ion battery has the highest energy density among secondary batteries for consumer use, it is expected that its energy density is far below the need of the future high-performance electronic devices. On the other hand, the energy density of hydrocarbon fuels such as methanol and butane is much larger than that of Li-ion battery. Therefore, miniaturized energy conversion system from chemical energy of hydrocarbon fuels to electricity attracts much attention [1].

The objective of the present study is to develop a micro-scale catalytic combustor, which is essential for various power generation principles such as external combustion engine, thermophotovoltaic, and reformer-based fuel cell. Our previous experiment using 0.6 mm ID tube showed that anodized nano-porous alumina is promising for the catalyst layer of micro-scale combustor [2]. Therefore, palladium (Pd) supported by the nano-porous alumina is employed as catalyst in the present study. A series of combustion experiments with normal butane (n-butane) fuel was made in a prototype combustor fabricated with high-precision ceramic tape-casting technologies.

2. Fabrication
2.1. Catalyst Layer

In the present study, catalyst support layer is nano-porous alumina made through anodic oxidation of aluminum layer. The advantages of the anodized alumina support are two folds; firstly, it is easy to optimize the film thickness and its characteristics such as porosity and pore diameter. Secondly, anodized alumina has good adhesion to the substrate, so that the catalyst layer is robust for thermal shock expected to occur in operation of micro combustors. Suzuki et al. [3] employed time-consuming thermal evaporation for the deposition of aluminum layer. In the present study, we employ thermal spray coating instead in order to fabricate thick aluminum layer efficiently. We also employ Pd catalyst, because Pd catalyst can be used up to 900 $^{\circ}$C, and has larger active surface area than Pt at higher temperature than 600 $^{\circ}$C.

Figure 1 shows the fabrication process of Pd/nano-porous alumina, which starts with deposition of 100 μm-thick aluminum onto the substrate using thermal spray coating. Then, the substrate is submerged into 4 wt% oxalic acid solution, and anodically oxidized at a current of 50 A/m^2 for 7 hours, followed by a bake at 350 $^{\circ}$C for one hour. Finally, the nano-porous alumina is dipped into diamine-dinitro-palladium solution at 50 $^{\circ}$C for 1.5 hours, and calcinated at 350 $^{\circ}$C for one

1. Anodic oxidation   3. Impregnation with Pd[(NO$_2$)(NH$_3$)]$_2$
   in (COOH)$_2$ (50 $^{\circ}$C, 1.5 h)
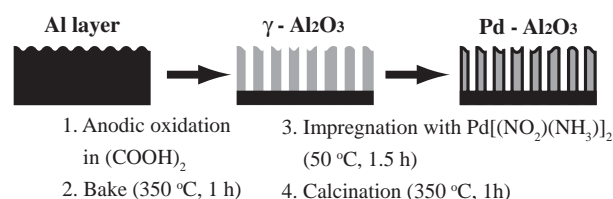2. Bake (350 $^{\circ}$C, 1 h)   4. Calcination (350 $^{\circ}$C, 1h)

Figure 1. Fabrication process of Pd/nano-porous alumina.

hour.

Figure 2a shows a SEM image of the aluminum layer deposited with the thermal spray coating. Since the aluminum particles employed have a diameter of around 20 μm, the surface roughness of the aluminum layer is a few tens of micrometers. After anodic oxidation, nano-porous alumina is obtained as shown in Fig. 2b, where the pore diameter and the mean spacing between pores are respectively 20 nm and 50 nm.

2.2. Ceramic Micro Combustor

In order to fabricate a cost-effective and robust micro-scale combustor, we employ high-precision tape-casting technology [3] developed for semiconductor ceramic packages by Kyocera Corporation. Its advantages are high heat resistance, applicability to quasi three-dimensional structure by stacking multiple layers, and simple integration of electrodes into the ceramic structure. In particular, the combustor fabricated by this technology can be operated at high temperature up to 800 °C, which is determined by the bonding temperature of ceramic plates.
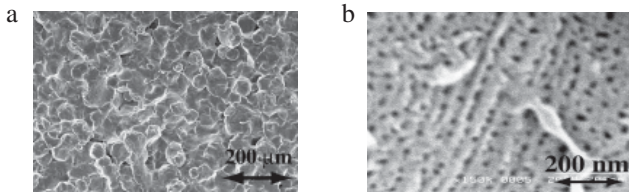
Figure 2. a:) SEM image of aluminum layer deposited with thermal spray coating. b:) SEM image of nano-porous alumina surface.
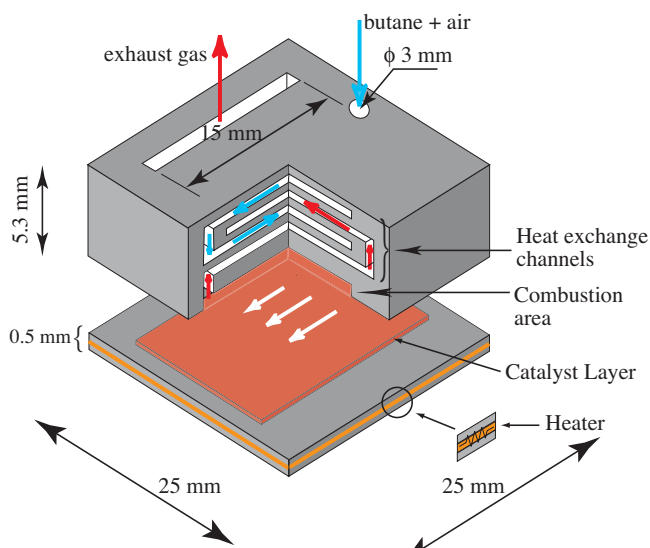
Figure 3. Schematic of micro-scale ceramic combustor with embedded heat exchange channels.

Figure 3 shows a schematic design of the micro-scale ceramic combustor. For heat recovery, this prototype combustor has cross-flow heat exchange channels whose heights are 0.5 mm. Through these channels, heat exchange takes place between the fresh mixture and high temperature exhaust gas. Surface reaction of *n*-butane occurs in the undermost combustion channel, of which dimensions are 15 x 19 x 0.3 mm^3. The present combustor is fabricated by stacking 12 ceramic plates; upper 9 plates for the heat exchange channels and the lower 3 plates for the combustion channel. The bottom plate has an embedded ignition heater and the electrodes for the anodic oxidation. Figure 4 shows a cross sectional view of the micro-scale ceramic combustor developed.

3. Combustion Experiment
3.1. Experimental Setup

Figure 5 shows a schematic of the present experimental setup. Flow rates of *n*-butane fuel and air are regulated by mass flow controllers. Fuel and air are fully mixed in the mixing section before entering the combustor. The combustor is submerged into a solder bath in order to keep the catalyst temperature constant at 200 - 400 °C. The fuel conversion
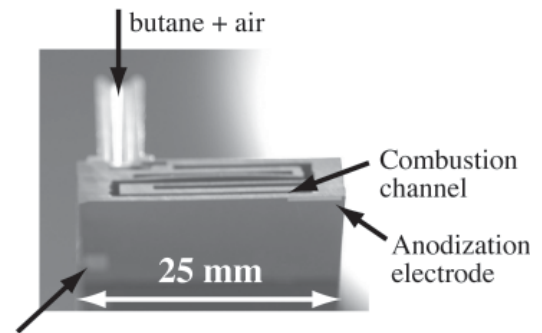
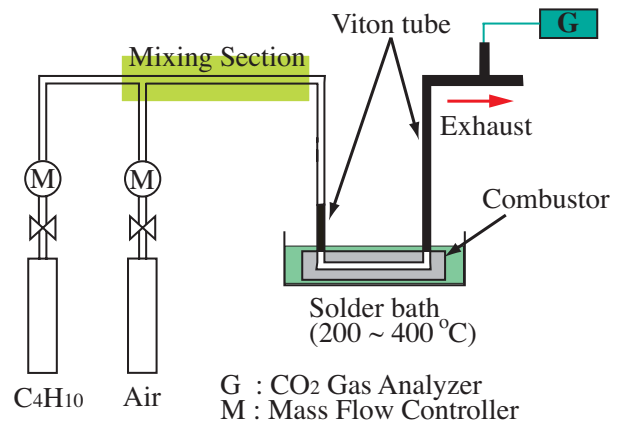Figure 4. Cross-sectional view of micro ceramic combustor.

Figure 5. Experimental setup.

efficiency is determined from carbon dioxide concentration in the exhaust gas. In the present experimental condition, the flow rate of n-butane Q_B is changed in the range of 2.5 - 5.0 sccm, which corresponds to the heat generation of 5 - 10 W at complete fuel conversion. The equivalence ratio ϕ is changed in the range of 0.5 - 1.0.

3.2. Experimental Results

Figure 6 shows heat generation versus the catalyst temperature. Onset of ignition is around 250 °C, and the heat generation increases with the catalyst temperature. When $Q_B =$ 2.5 sccm and ϕ =1.0, complete fuel conversion is achieved with 5 W heat generation at 400 °C. Under this condition, heat generation density is as large as 58 MW/m³. When $Q_B =$ 5.0 sccm and ϕ =1.0, the fuel conversion efficiency is about 90 % at 375 °C. Therefore, even if we employ Pd catalyst instead of Pt, we can obtain high heat generation density at 400 °C. In addition, reduction of the equivalence ratio from 1.0 to 0.5, which corresponds to the decrease in the residence time, gives small changes on the fuel conversion efficiency. This indicates that diffusion in the combustion channel is not the limiting factor, so that the surface reaction speed itself plays a dominant role in determining the overall reaction rate.

4. Modeling and CFD Analysis
4.1. Surface Reaction Model

Detailed mechanism of n-butane surface reaction remains unknown because of its complex elementary reaction steps. On the other hand, some simple and reasonable reaction models are proposed for hydrocarbon fuels such as methane [4]. In the present study, we assume one-step irreversible reaction of n-butane, i. e.,

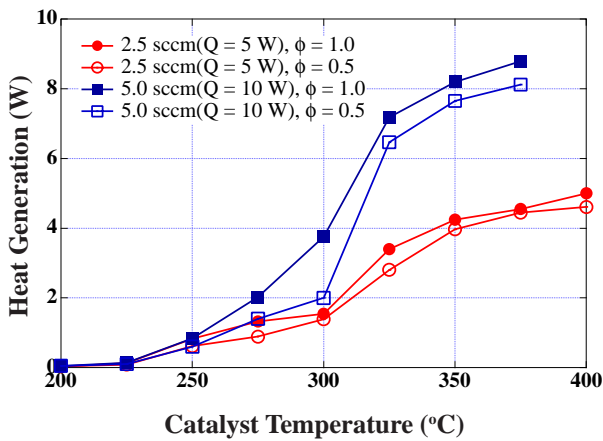$$C_4H_{10} + 6.5O_2 \rightarrow 4CO_2 + 5H_2O. \qquad (1)$$

Figure 6. Heat generation versus catalyst temperature.

In addition, since the oxidation rate of hydrocarbons on catalyst is typically modeled as the first order in fuel concentration and independent of oxygen concentration [5], the surface reaction rate of n-butane R_B can be expressed as

$$R_B = C_{B,s} \cdot A \cdot \exp\left(-\frac{E}{RT}\right), \qquad (2)$$

where $C_{B,s}$, A, E, R, and T are respectively molecular concentration of butane at the catalyst surface, pre-exponential factor, activation energy, universal gas constant, and catalyst temperature. We should determine the reaction constants, A and E, based on the experimental data. In the present study, we use the 1-D plug flow model, where no mixing in the flow direction but perfect mixing in the cross-stream direction is assumed. From a mole balance equation of n-butane and Eq. (2), we obtain

$$A \exp\left(-\frac{E}{RT}\right)$$
$$= -\frac{uA_c}{WL}\ln\left(\frac{C_{B,b}(L)}{C_{B,b}(0)}\right)\bigg/\left[1 + \frac{uA_c}{Wk_{m,B}L}\ln\left(\frac{C_{B,b}(L)}{C_{B,b}(0)}\right)\right], \quad (3)$$

where u, A_c, W, L, $C_{B,b}(x)$, and $k_{m,B}$ are respectively bulk mean velocity, cross-sectional area of the combustion channel, wetted area per unit length, streamwise length of the catalyst layer, bulk mean concentration of n-butane at the streamwise position of x, and mass transfer rate of n-butane [2]. In the derivation of Eq. (3), the bulk mean velocity is assumed constant through the combustor, and the mass boundary layer is assumed fully developed with Sherwood number equal to 4.

We can determine all the variables in the right hand side of Eq. (3) from the combustor dimensions and the experimental results. Figure 7 shows the R. H. S. of Eq. (3) versus $1/T$. The
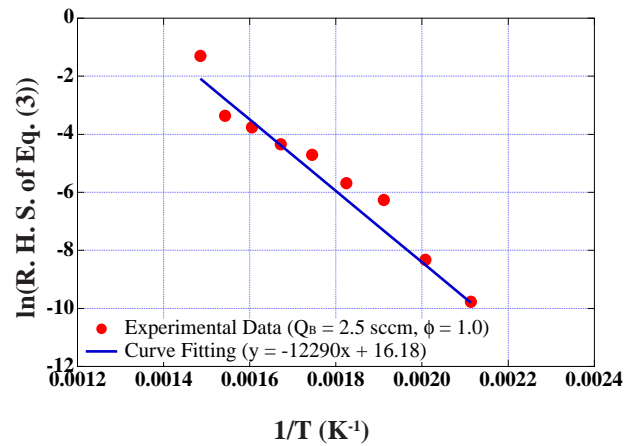
Figure 7. Temperature dependence of the specific reaction rate using the experimental data for Q_B = 2.5 sccm and ϕ = 1.0.

symbols are the experimental data for $Q_B = 2.5$ sccm and $\phi = 1.0$. By a least-square method using the data between 200 - 400 °C, we obtain the reaction constants as follows: $A = 1.061 \times 10^7$ (m/s) and $E = 1.022 \times 10^8$ (J/kmol).

4.2. CFD Analysis of the Ceramic Combustor

With the reaction constants in the surface reaction model, we make a series of CFD analysis with a commercial software (Fluent 6, Fluent Inc.). In addition to the Navier-Stokes equations and the energy equation, species transport and heat conduction equations in the ceramic wall are solved. The temperature of the catalyst is set constant, and all the external surfaces of the combustor excluding inlet and outlet are thermally insulated. The temperature of the inlet gas is 27 °C. In addition, thermal conductivity of the ceramics is set to 14 W/(mK). The bulk Reynolds number is 6 - 34, and flow inside the combustor remains laminar. The experimental data are compared with the CFD results in Figs. 8 and 9. Figures 8 and 9 show the comparison at $Q_B = 2.5$ sccm and 5.0 sccm,
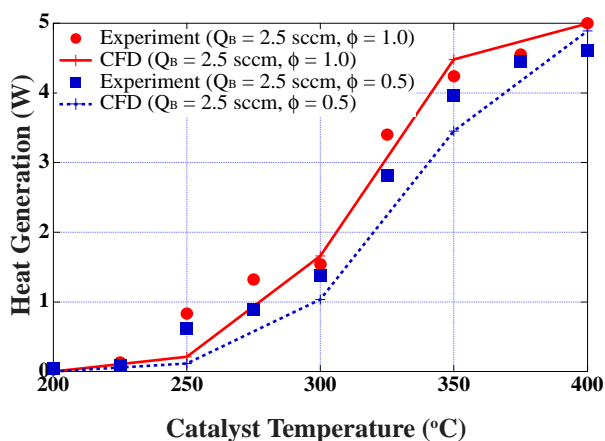

Figure 8. Comparison between experimental data and CFD results at $Q_B = 2.5$ sccm.
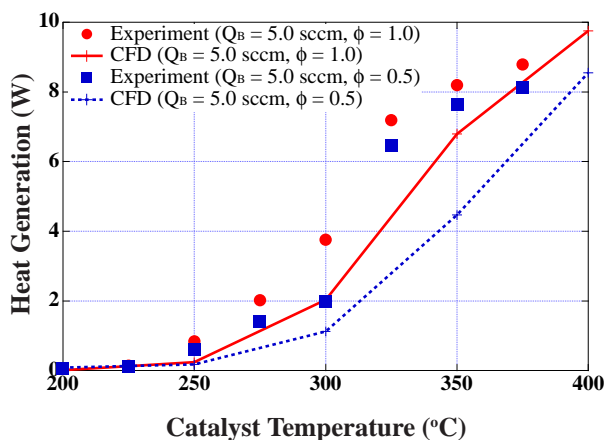

Figure 9. Comparison between experimental data and CFD results at $Q_B = 5.0$ sccm.

respectively. When $Q_B = 2.5$ sccm and $\phi = 1.0$, the CFD results are in good agreement with the experimental data. On the other hand, the CFD results underestimate the heat generation especially for $Q_B = 5.0$ sccm and $\phi = 0.5$. The reason of this disagreement is now under investigation.

It is also found that when $\phi = 1.0$, complete fuel conversion can be obtained up to $Q_B = 35$ sccm at 800 °C, which is the upper temperature limit of the present combustor (not shown).

5. Conclusions

Micro-scale catalytic combustor is successfully developed using a high-precision tape-casting technology. Pd/nano-porous alumina catalyst is found to work well for micro-scale catalytic combustion of *n*-butane. In particular, the aluminum layer fabricated by thermal spray coating shows availability for catalyst support after the anodic oxidation. Pd catalyst shows high activity even at low temperature around 400 °C. CFD analysis suggests that when $\phi = 1.0$, up to 35 sccm *n*-butane is completely converted at 800 °C with the present combustor.

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