Scaling Issues of Micro Catalytic Reactors

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Abstract. Micro catalytic combustors are studied experimentally. Microchannels, coated with Pt catalytic walls and columns were fabricated to investigate microscale catalytic reaction. This microscale reaction enhancement by Pt catalytic surface area is characterized by increasing outlet gas temperature with the increase of surface-to-volume ratio. It is found that the reaction efficiency improvement by Pt catalytic columns will extend the operation conditions especially for smaller microchannel size.

Introduction

The development of Micro/Nano technology in the last ten years has spurred interest in the realization of combustion at scales much smaller than previously explored. However, combustion at microscale faces numerous challenges. Today we know that reaction will quench when size of reactor is smaller than quenching distance. The reasons leading to quench include higher surface-to-volume ratio (S/V), radical quenching on wall, and competition of different timescales. As devices are scaled down, S/V ratio becomes larger. It means heat is being lost faster than it is being produced. On the other hand, smaller reactor will increase collision frequency of gas molecules to wall. Radical depleted by wall will cause discontinuity of reaction and flame quenching. Since it is difficult to counteract heat loss mechanisms due to facts of high S/V ratio at microscale, an innovative way to look at this problem is to increase rapidity of heat release. Catalyst was used to reduce activation energy barrier and increased reaction rate. Catalytic combustion is ideally suited to provoke faster combustion by taking advantage of high surface areas at microscale. Several groups are developing micro catalytic chemical reactor by using microfabrication technology. These include micro IC engines \cite{1} and micro gas turbines \cite{2}. A common micro catalytic reactor design is a microchannel device equipped with catalytic wires and catalytic walls for highly exothermic reaction \cite{3}. Such systems have feature sizes in sub-millimeter ranges and reaction components can be further integrated with sensors. Lots of efforts were also developed to improve thermal management. For example, \textquotedblleft Swiss Roll\textquotedblright \cite{4} and multi-quartz tubes\cite{5} utilized insulated conditions to reduce heat loss from reactor. After reaction occurs in reactors, it is difficult to get information in reactors. Some numerical studies \cite{6} provided influences of heat transfer and flow field to reaction. Maruta et al.\cite{7} computationally investigated the extinction limits of catalytic combustion in microchannels. Two types of extinction limits, a heat-loss induced limit at low velocity and a blow-off type limit at higher velocity, have been reported in their study.

The present efforts of this research are to study the effects of S/V ratio, fuel concentration, and flow velocity on combustion efficiency, as well as timescale competition of microscale combustion experimentally and theoretically. In experiments, microchannels with varying S/V ratios were designed and fabricated. In order to characterize micro reactors, integrated temperature sensors and a 25\textmu m R-type thermocouple were used to measure surface temperature on channel wall and gas temperature at outlet. Theoretical analysis provided some views to define timescales and conversion ratio at different operation conditions, which help us to better understand the physics of microscale catalytic reactor.
Theoretical Analysis

The major issues in microscale combustion are competition of timescales. Important timescales include residence time ($\tau_r$), diffusion time ($\tau_d$), and reaction time ($\tau_c$). Damköhler number is ratio of residence time and reaction time. For a completed reaction, relation between three timescales should be $\tau_c < \tau_d < \tau_r$. However, residence time may be greater than diffusion time or reaction time in a micro reactor. The competition between residence time and diffusion time influences conversional efficiency because diffusion is an important process for catalytic combustion. Eq.4 is used to estimate these timescales. Residence time equals to length ($L$) of micro reactors divided by flow velocity ($U$). Diffusion time depends on diffusivity ($D_{AB}$) and diffusive length ($d_H$). Diffusivity ($D_{AB}$) is function of species and temperature. The reaction time depends on the Arrhenius law no matter surface or gas phase reaction. The estimated timescales will be showed in discussion.

$$\tau_r = \frac{\text{microchannel length}}{\text{average velocity}} = \frac{L}{U}$$  \hspace{1cm} (1-a)

$$\tau_d = \frac{d_H^2}{D_{AB}}$$  \hspace{1cm} (1-b)

$$\tau_c = \frac{\text{fuel}}{\text{fuel consumption rate}}$$  \hspace{1cm} (1-c)

Design, Fabrication and Experimental Setup of Micro catalytic reactor

Catalytic reactor requires integrating several micro devices into a system, including microchannels, catalytic walls/columns, and temperature sensors. Fig. 1(a) shows the design of micro catalytic reactor. The micro catalytic reactor consists of a microchannel with catalytic walls/columns, and sealed from bottom by a glass wafer with temperature sensors. The microchannel, 1mm wide, 20mm long with 1.0, 0.4 or 0.04 mm deep, and integrated with catalytic walls/columns and temperature sensors, were fabricated by using MEMS technology. There are total 8 temperature sensors located from inlet to outlet of micro catalytic reactor. The less than 1.0 mm heights of micro catalytic reactor were chosen because these sizes are smaller than quenching distance of hydrogen-air combustion and because it is comparable to sizes proposed in many micro reactors. Fig. 1(b) shows the cross sectional view of A-A cut in a micro catalytic combustion. The micro catalytic reactor consists of two parts: the microchannel plate and the temperature sensor plate. The microchannel plate is an etched channel with electroplating nickel columns coated with platinum (Pt) on their surfaces. Pt acts as catalyst in hydrogen/air oxidation reaction. The temperature sensor plate has Pt thin film metal patterned by lift-off technique. Since resistance of platinum increases linearly with rising temperature, they can serve as temperature detectors within micro catalytic reactors. Detailed microfabrication processes are described elsewhere [8]. The catalytic columns are 25 $\mu$m in width, length and spacing and heights of 10, 17, 31, 53, and 78 $\mu$m. Fig. 2 and Fig. 3 show images of micro temperature sensors and Pt catalytic column array and photograph of micro catalytic combustor.
Fig. 2 Photograph of (a) micro temperature sensors and (b) micro catalytic columns

Fig. 3 Photograph of MEMS-fabricated micro catalytic combustor

Fig. 4 Experimental setup includes: (i) micro catalytic reactor chip, (ii) hot plate (iii) reaction gas supply facilities (iv) mass flow meters

Fig.4 shows the experimental setup. Experimental setup consists of a catalytic reactor chip\textsuperscript{(i)} mounted on a hot plate\textsuperscript{(ii)}. The maximum temperature of the hot plate can reach 450°C. Compressed gas tanks\textsuperscript{(iii)} are used for the supply of the reactant gases. Mass flow meters\textsuperscript{(iv)} are used to manipulate the H\textsubscript{2} and air flow rates. Reactant gases are premixed before entering into micro reactor.

Experiments are conducted by supplying reaction gases into a micro catalytic reactor which is preheated by a hot plate\textsuperscript{(ii)}. During experiments, hot plate is kept at a fixed temperature and whole chip is thermal insulated by using asbestos. Wall temperature is measured by using integrated temperature sensors and gas temperature at outlet by a R-type thermocouple. To convert resistance changes of temperature sensors to voltage output, constant current circuits are custom-built. Output voltage is digitized by A/D converter in a personal computer.

**Experimental Results and Discussion**

**1) Limits of operation conditions**

Parallel studies of combustion in catalytic micro-tubes by Chao et al. [9] have proposed limits of operational conditions, as shown in Fig.5, for micro catalytic reactors. Fig.5 has been used to describe operational conditions in current experiments. According to Chao’s paper, upper limit of fuel concentration depends on maximum amount of heat release, for example, stoichiometric equilibrium ratio because fuel concentration more than stoichiometric ratio can’t support any more energy. The upper limit of flow velocity depends on sonic speed. Increasing flow velocity will cause problems such as chocked flow, pressure loss, and competition of different timescales. Chocked flow may occur due to chocked nozzle or shear stress effects. Fano line effect [10] shows that subsonic inner flow field will be accelerated due to friction led by shear stress. Chocked flow occurs as the flow velocity is accelerated to Mach number = 1. Line A is according to Eq.3, so the area below curve
A is the ratio of heat generate over heat loss less than 1. It means no excess energy can be obtained in the area. Actually curve A is function of fuel concentration, flow velocity, combustion efficiency, and heat loss. If one can improve combustion efficiency and heat loss, curve A will move to left and down direction in the figure. The conditions in area above curve A are the reaction zone area. Curve B is catalytic microscale combustion limit.

In right side of curve B area, much shorter residence time compared with reaction time or diffusion time \((\tau_r \ll \tau_c \text{ or } \tau_r \ll \tau_d)\) results in reaction extinct due to not enough residence time for chemical to react (or diffuse) on catalyst walls. Therefore, curve A and curve B form an area where reaction occurs. Curve C is used to separate inside reaction and outside reaction of micro catalytic reactors. The former means the reaction inside microchannel such as surface reaction, and the latter means gas phase reaction when excess reactant gases react behind the exit. Curve C can be considered as the competition of residence time and diffusion time. Curve A, B, and C will move to the right and upper side in the figure as decreasing microchannel size (or increasing surface-to-volume ratio) because the flow velocity and fuel concentration should be increased to overcome the heat loss. The area formed by curve A, B, and C will disappear for decreasing microchannel size (or increasing surface-to-volume ratio). It is obvious that operational conditions will become narrower and finally become a point Q which depicts ultimate size limit of micro catalytic reactor.

**Figure 6** Estimated timescales for experiments in (a) H=1, 0.4, 0.04mm with catalytic walls only. \((T_o = 533K, H_2: 75 \text{ SCCM and Air: 188 SCCM})\) (2) H=0.4mm with catalytic walls and columns \((T_o = 533K, H_2: 64 \text{ SCCM and Air: 172 SCCM})\)

(2) **Estimation of timescales**

Residence time \((\tau_r)\) is defined as volume/volumetric flow rate in Eq.(1a). At a fixed flow velocity \(U\), residence time \((\tau_r)\) is equal to channel length \((L)\) of micro reactor divided by flow velocity \((U)\). Diffusion time \((\tau_d)\) is estimated as diffusion length square/diffusion coefficient \((d_0^2/D_{AB})\) in Eq.(1b). Diffusion length \((d_0)\) is determined by the distance between centerline and catalyst wall (or one-half height of columns) in microchannels without (or with) catalytic columns. The diffusion coefficient \((D_{AB})\) is estimated by using average \(O_2\) diffusion coefficients between maximum and minimum temperatures. \(O_2\) diffusion coefficient is used because of its slower diffusion velocity. Reaction time \((\tau_c)\) is defined as fuel/fuel_consumption_rate in Eq.(1c) and can be estimated from simulation tools with the same outlet gas temperature from experimental results.

**Figure 6** shows estimated diffusion, residence and reaction timescales for experiments within (1) H=1, 0.4, 0.04mm microchannel with catalytic walls only, but no micro columns as wall temperature \(T_o\) is preheated at 533K while flow rates of \(H_2\) and air were kept at 75 SCCM and 188 SCCM. (2) H=0.4mm microchannel with catalytic walls and columns as wall temperature \(T_o\) is preheated at 533K while flow rates of \(H_2\) and air were kept at 68 SCCM and 172 SCCM. The estimated
timescales are plotted as a function of surface-to-volume (S/V) ratio in Fig.6. For H=1, 0.4 and 0.04mm microchannels without micro catalytic columns, S/V ratio increases from 4 to 7 and 52 mm\(^{-1}\). Damköhler number, defined as ratio between residence time and characteristic reaction time, is about 220 for H=1mm microchannel, 40 for H=0.4mm microchannel, and reduces to 3 for H=0.04mm microchannel experiments. Damköhler number is used to determine reaction can be happened or not. Thus, the competition of reaction time with residence time and diffusion time would become major issues for H=0.04mm microchannel if residence time is further reduced by increasing flow velocity.

**Summary**

The catalyst used for microscale combustion is feasible and can take place the reaction in a 400µm height microchannel which is below the quenching distance 600µm. The competition of time scales is important in the study, the results show that Damköhler number influences the reaction exist or not and the competition of residence time and diffusion time influences the reaction form and catalytic combustion efficiency. To improve the combustion efficiency and heat loss problem can extend the operational conditions especially for smaller channel size and avoid the operational conditions covering the competition of time scales.

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**References**


