# Effect of Catalyst Segmentation with Cavities on Combustion Enhancement of Multi-Fuels in a Micro Channel

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### **1** Introduction

Hydrocarbon-fueled micro-reactors have received increased attention as a potential means of energy conversion for electrical power generation in portable electronics due to their superior energy density compared to that of state-of-the-art lithium batteries [1]. Conversion of chemical energy of fuels into electricity in a microscale device without moving parts can be achieved by using fuel cells, photovoltaics [2] and thermoelectrics [3]. A major obstacle in creating practical micro-reactors (with characteristic dimension < 1 mm) is their enhanced heat loss and combustion instability. Homogeneous flames are typically quenched when confined in spaces with dimensions below their quenching distances [4]. The associated large surface-to-volume ratio of the micro-reactor calls for the potential applications of the heterogeneous conversions and the heterogeneous catalytic combustion in a micro-reactor received intensive research attentions recently [5, 6]. Complicated heterogeneoushomogeneous interactions can be observed in the microreactors. Well-know aspects of interactions include the promotion of gas-phase reactions due to the catalytically induced exothermicity and the inhibition of gaseous reactions due to the competition of fuels and oxidizers by the catalyst bed. This competition between heterogeneous and homogeneous reaction often leads to incomplete combustion and narrowing of the stable operating range. Therefore, some strategies were proposed to implement in micro-reactors, such as heat recuperation [7] and utilizing quench-resistant fuels [8]. Pertinent design of combustor configuration and catalyst bed can result in improvement of reaction and heat and radical loss in the reactor. Federici et al. [7] demonstrated that the thermal properties of reactor materials play a vital role in the overall thermal stability of micro-reactor. The reactor walls not only account for the heat loss through conduction, but they are often responsible for the majority of the heat transfer from upstream, which is necessary to preheat the feed to ignition temperature. In other words, a proper manner to maintain high wall temperature in localized space can extend gas reaction and mitigate radical quenching. Moreover, Norton and Vlachos [8] report that adding hydrogen can successfully

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induce self-ignition of propane/air mixtures (gas reaction) in the microreactor with capitalization on the heterogeneous reaction of hydrogen. Accordingly, when burning the multi-fuels of carbon monoxide and hydrogen blending with hydrocarbon in a catalytic micro-reactor will definitely exhibit complicated hetero- and homogeneous reaction based on their different diffusive and catalytic characteristics. Nevertheless, the interplay of kinetics and transport of multi-fuels reactions in the catalytic micro-reactors is scarcely studied in the past.

To mitigate the inhibition and to promote complete combustion, catalyst segmentation in a hydrogen microreactor was proposed by our group [9]. In this setup the heterogeneous reaction on a prior catalyst is to assist the downstream homogeneous reaction by providing sufficient chemical radicals and catalytically induced exothermicity. Subsequently, the following sequentially-segmented catalyst inherits the heat and chemical radicals from upstream, and contributes to further deplete hydrogen in residual combustible mixture till complete conversion. In this approach, the cooperation between hetero- and homogeneous reaction replaces the inhibition competition, and moreover, catalyst segmentation distributes the overall catalytic exothermicity on the wall, that will benefit to reduce the hot spots and damage to the wall materials.

Traditionally, the stable operating range of the microreactor is restricted to low inlet velocities (less than 1 m/s) [6-8]. To extend the operation range and to study into the interplay of  $H_2/CO/CH_4$  multifuels reactions in a catalytic micro-reactor, a novel catalyst bed design of catalyst segmentation with cavities is proposed and demonstrated in the following sections.

### 2 Numerical model and chemical mechanism

In this work, a commercial code, CFD-ACE is modified to incorporate with detailed gas-phase and surface reaction mechanisms in CHEMKIN formats to simulate the flow and reaction characteristics inside a micro channel. For simplicity, the micro reactor is modeled as a two dimensional system with a gap width (L) of 1mm between the two parallel plates in the numerical simulation. Figure 1 shows the schematic of the catalytic micro channel modeled in this work, and simulations are performed in one half of the channel for symmetry. The reactor is 3cm in length with the wall thickness of 0.2mm. The concept of catalyst segmentation with cavities is proposed and demonstrated for multi-fuels reaction enhancement in this study. The catalyst segment is coated with platinum. The cavity width is 1mm and the cavity depth is 0.2mm.

For boundary conditions, the stoichiometric fuel-air mixture is specified at the inlet. Three different multi-fuels compositions are studied:  $50\%H_2+50\%CO$ ,  $50\%CH_4+50\%CO$ ,  $50\%CH_4+50\%H_2$ . The inlet temperature for the fuel/air mixture is 300K. A uniform velocity profile of 10 m/s is specified at the inlet and the flow field is laminar for all cases studied. The thermal boundary condition at the wall is the heat loss to the ambient air at 300K. The exterior heat loss is the heat convection by air. At the exit, pressure is specified with a constant ambient pressure of 101 kPa and an extrapolation scheme is used for species and temperature.

Grid independence has been examined and a non-uniform mesh with the distribution of  $211\times65$  grid points in the axial and transverse directions is used. The simulation convergence is decided when the residuals of all governing equations approaches steady states with residuals smaller than  $10^{-4}$ . Detailed gas-phase and catalytic surface reaction mechanisms are applied. GRI-Mech 3.0 mechanism is used for gas-phase reaction and the surface reaction mechanism is compiled primarily from that proposed by Deutschmann et al. [10].

# **3** Results and discussion

### Hydrogen and carbon monoxide mixture

Hydrogen and carbon monoxide have relatively high sticking coefficients to platinum catalyst. However, hydrogen has inherently large mass diffusivity compared to carbon monoxide, so that hydrogen would deliver to catalyst bed and trigger the heterogeneous reaction first. Figure 2 shows the

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computed contours of fuels and OH radical mass fraction at an equivalence ratio of 1.0 and inlet velocity 10 m/s in case of multi-segment catalyst (top) and multi-segment catalyst with cavities (bottom). No significant difference in results between two catalyst configurations is observed. Once the inlet velocity is increased to 30 m/sec, the gas reaction in multi-segment catalyst case will extinguish caused by strong flow rate and sequentially eliminate the surface reaction due to gradually decreasing surface temperature. On the contrary, gas reaction is anchored in the cavity and surface and gas reactions in cooperation maintain a high wall temperature. Figure 3 shows the fuel and OH mass fractions along the centerline at inlet flow rates of 10, 20 and 30 m/s. It appears that hydrogen attains complete conversion prior to CO conversion, and then the onset of gas reaction recedes downstream with an increase of flow velocity.

Hydrogen tends to lightoff early on the surface, and provides catalytically induced exothermicity and profound chemical radicals to support the hetero-/homogeneous reaction of carbon monoxide. Besides, the Lewis number of hydrogen is about 0.287, which is much smaller than that of CO (1.09). It means that hydrogen is responsible for stabilizing gas reaction in high flow velocity due to high mass diffusivity.

### Methane and carbon monoxide mixture

As regards methane and carbon monoxide mixture, they have similar Lewis number, but CO has a high sticking coefficient to platinum. Multi-segment catalyst sustains gas reaction in the microchannel. Figure 4 shows that methane can evidently deplete in first two catalyst segments, but incomplete combustion yields high concentration of CO species. Upstream heterogeneous reaction provides chemical radicals and exothermicity, and homogeneous reaction benefits to expedite dissociation of fuel species, but very short residence time leads to high CO concentration in residual gas. Subsequently, the following sequentially-segmented catalyst contributes to deplete CO in residual combustible mixture till complete conversion. In the case with cavities, the gas reaction moves upstream and anchors in the first cavity. Furthermore, it takes a shorter distance to attain relatively high conversion. Figure 5 indicates the fuel and radical mass fraction distributions in first 2 mm distance from the entrance. In first 1mm distance, methane depletes in the catalyst segment and yields CO and CH<sub>3</sub> species due to dissociation of methane. In the following 1 mm, the OH distribution in the cavity implies gas reaction existing so that CH<sub>4</sub> and CH<sub>3</sub> can further deplete in this region. On the contrary, high flow velocity postpones the onset of gas reaction in the multi-segment catalyst case so that methane mass fraction is increasing due to mass diffusion from mainstream. Although methane yields carbon monoxide due to incomplete combustion, OH and H radicals from gas reaction promote CO depletion. The chemistry formula of CO+OH $\rightarrow$ CO<sub>2</sub>+H in gas reaction is more active than that of  $CO+O_2 \rightarrow CO_2$  in surface reaction. In other words, CO surface reaction dominates in the first catalyst segment, and provides exothermicity to pre-react methane. Methane releases H and OH radicals to assist CO conversion in the following gas reaction.

### Hydrogen and methane

With regard to hydrogen and methane mixture, there is no gas reaction in the multi-segment catalyst microreactor in stoichiometric condition and inlet velocity of 10 m/sec. However, gas reaction can stabilize in the case with cavities. Comparing with the  $CH_4/CO$  results above, hydrogen in  $CH_4/H_2$  mixture provides much smaller volumetric energy density (0.0108 MJ/L). In a high flow velocity condition, catalytically induced exothermicity from hydrogen in single and multi-segment catalyst cases is unable to ignite gas reaction of methane due to low energy density and heat loss. Nevertheless, cavity plays an important role to decelerate the flow velocity in localized space and collect radicals from upstream. Figure 6 shows the fuel and radical mass fractions in multi-segment catalyst with cavity case. Apparently, reactions in the cavity stabilize a main gas reaction in the channel. As shown in Fig. 7 of the mass fraction distribution, methane is consumed in two stages in 2mm from entrance. The first stage within the first 1mm region is dominated by heterogeneous reaction of the catalyst, while the second stage in the next 1mm region is responsible for gas reaction anchoring in cavity. Temperature leap and OH radical congregation imply gas reaction in the cavity. Hydrogen is reduced

first in the catalyst section, and abruptly rises in the cavity section caused by dissociation of methane. As regards CO mass fraction, there is a broadband distribution in two sections. Accordingly, incomplete combustion of methane releases high CO concentration.

High wall temperature maintaining in a high flow velocity case is an essential key to sustain gas reaction in microreactor. In view of low volumetric energy density but high mass diffusivity of hydrogen, to diminish heat loss and to provide a stable heat source on the wall are important to have high chemical conversion. Consequently, it notes that hydrogen concentration in  $CH_4/H_2$  mixture and wall properties are important design parameter in this case.

# 4 Conclusions

In this paper, the effects of the proposed novel design of catalyst segmentation with cavities on  $H_2/CO/CH_4$  multi-fuels combustion enhancement in a micro-reactor are investigated by numerical simulation with detailed heterogeneous and homogeneous chemistries of methane, carbon monoxide and hydrogen. Numerical results reveal that the heterogeneous reaction in the prior catalyst segment can produce active chemical radicals and catalytically induced exothermicity, and homogeneous reaction is subsequently induced and anchored in the following cavity. CO/H<sub>2</sub> mixture can sustain in high flow velocity in two catalyst configurations caused by their high sticking coefficients, so that  $CO/H_2$  can lightoff on catalyst segment.  $CO/CH_4$  mixture can be stabilized in high flow velocity in two catalyst configurations. In the upstream catalyst segment incomplete combustion of methane yields carbon monoxide, and, the following catalyst segments fully consume carbon monoxide due to the preferred CO catalytic reaction of high sticking coefficient on the platinum surface. Furthermore, OH and H radicals from methane also enhance CO gas reaction by switching chemical pathway. As regards CH<sub>4</sub>/H<sub>2</sub> mixture, only multi-segment catalyst with cavity can stabilize gas reaction in a high flow velocity. Cavity can collect radicals and maintain wall temperature, so that it can successfully sustain gas reaction in a high flow velocity even though hydrogen provides low volumetric energy density. These processes of multi-fuel catalytic combustion belong to mutual assisting coupling between the heterogeneous and homogeneous reactions, instead of mutual competing in a conventional catalyst reactor. In this way, fully methane conversion and complete combustion can be accomplished in a short distance, so that the system can be further scale-downed. The existence of the cavity can appreciably extend the stable operation range of the multi-fuel micro-reactor in a wide variety of inlet flow velocities. These outstanding features of this catalyst configuration facilitate wide applications in various small-scale power/heating generation systems.

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Fig 1. Schematic of computational domain.



Fig. 2. Computed contours of (a)  $H_2$ , (b) CO and (c) OH mass fraction in color code with equivalence ratio 1.0 and inlet velocity 10 m/s in cases of segmented catalyst (top) and segmented catalyst with cavities (bottom).



Fig. 3. (a) Fuels ( $H_2$  and CO), and (b) OH mass fractions along the centerline for segmented catalyst with cavities condition in varied flow velocity..



Fig. 4. Computed contours of (a)  $CH_4$ , (b) CO and (c) OH mass fraction with equivalence ratio 1.0 and inlet velocity 10 m/s in cases of segmented catalyst (top) and segmented catalyst with cavities (bottom).



Fig. 5. (a) Fuels (CH4 and CO), and (b) radicals mass fraction for segmented catalyst and segmented catalyst with cavities condition in first 2 mm distance from the entrance.



Fig. 6. Computed contours of (a) fuel and (b) radiacl mass fraction with equivalence ratio 1.0 and inlet velocity 10 m/s in cases of segmented catalyst with cavities.



Fig. 10. (a) Temperature, fuels (CH4 and H2) and (b) radicals mass fraction for segmented catalyst and segmented catalyst with cavities condition in first 2 mm distance from the entrance.