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Full Length Article

Heterogeneous reaction characteristics and its effects on homogeneous combustion of methane/air mixture in microchannels II. Chemical analysis

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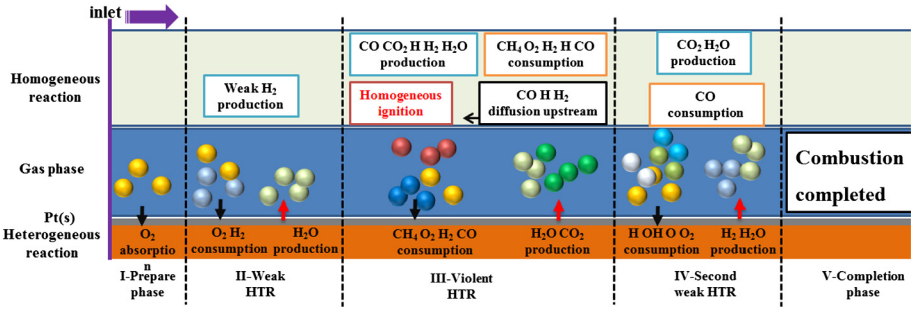
GRAPHICAL ABSTRACT



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ABSTRACT

Catalytic combustion of methane/air mixture in various channels was numerically investigated to illuminate the chemical interaction mechanism between heterogeneous reactions (HTRs) and homogeneous reactions (HRs) with detailed gas-phase and surface reaction mechanisms. In the channels of different widths and with/without catalyst, the gaseous species, such as CH_4, O_2, CO, CO_2, H, H_2, and H_2O and the reactions involving these species were monitored and the reaction rates along the streamwise direction were analyzed quantificationally. In the catalytic combustion, the HTR can be divided into prepare phase, weak HTR phase, violent HTR phase, second weak HTR phase, and completion phase according to the situation of gaseous species depletion on catalytic surface. The heat released by the homogeneous reaction and the consumption of O(s) can accelerate the absorption of CH_4 on Pt surface in the violent HTR phase (phase III). Meanwhile, the stronger competition to CH_4 of HR would inhibit the reactions of HTR involving CH_4. The similar situation happens to O_2, except the larger consumption of O_2 by HTR than that of CH_4 because of the larger stick coefficient of O_2 on Pt surface. The additional reaction pathway of CO through HTR is favorable for the completeness of CO to CO_2 during combustion. The consumption of H radical by HTR in the second weak HTR phase (phase IV) leads to the H_2 release from Pt surface to the gas-phase and promotes the homogeneous reactions. The decrease of the width of the channel would suppress the HR intensity and enhance the HTR intensity. However, HR is still dominated in all the cases with a large amount of CH_4 and O_2 consumption and CO_2 and H_2O production.

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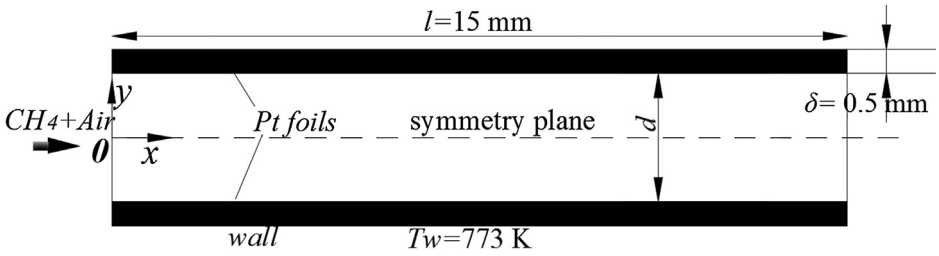

Fig. 1. . Schematic of micro channel.

1. Introduction

Micro combustion has been investigated widely due to its low cost, high density, and being friendly to the environment [1]. However, problems such as the stability and efficiency maybe huge obstacles in the practical use because of the increasing heat loss and inadequate residence time for fuels and oxidizers in micro combustion. Catalytic combustion is an effective method to overcome these challenges above due to its more stable operation, low ignition temperature, and less heat loss [2–4]. Lots of researches of catalytic combustion in microscale have been carried out in recent decades [5–15]. Still, it is complex and not easy to understand because of the co-exist of homogeneous and heterogeneous reaction in catalytic combustion. The heat released by homogeneous and heterogeneous reactions may promote the process of each other by affecting the ignition, reaction, and quenching process. Meanwhile, the chemical interaction between heterogeneous and homogeneous reaction is also complex because there are reactants and intermediates are consumed or released by the two kinds of various reactions in different combustion stages, leading to the hard judgments of prohibition or enhancement effect for each other.

To understand the chemical interaction between homogeneous and heterogeneous reaction, researchers have conducted lots of chemical analysis of catalytic combustion. Ciuparu et al. [16] investigated the fate of hydroxyls at the surface of γ-Al2O3 supported palladium oxide catalysts under lean methane combustion reaction conditions by using in situ diffuse reflectance-fourier transform infrared (DR-FTIR) spectroscopy. They found that hydroxyls was formatted and accumulated at the catalyst surface during the oxidation and the oxygen mobility of the support influenced the dynamic behavior of hydroxyls at the surface. OH^* concentration in narrow channels was measured by OH-PLIF in methane/air combustion, and the low concentration of OH confirmed the radical quenching effect of wall [17]. Using situ spatially-resolved Raman measurements and planar laser induced fluorescence (LIF), Sui et al. [18] assessed the catalytic combustion processes of fuel-rich CH_4/O_2/N_2/CO_2 mixtures on Pt and Pd at 5 bars. It was found that the higher H_2 production of Rh had a profound impact on gaseous combustion and Pt suppressed homogeneous reaction.

While it is not easy to illuminate the chemical interaction mechanism in catalytic combustion due to the limitation of the capability and accuracy of experimental measurements, the CFD method with appropriate models can predict the species concentration and temperature distribution in combustion [19–24]. Chen et al. [25,26] constructed contribution diagrams and made design recommendations by comparing the combustion performance under different operating conditions in a two-dimensional model. The radical flux inhibition on homogeneous ignition caused by heterogeneous reaction was reported in Appel et al.'s work [27]. The combustion products, like H_2O has a suppression effect in H_2/air catalytic combustion [6]. The suppression mechanism was elucidated by Bui et al. [28]. Additional OH radical can promote fuel conversion rate in catalytic combustion [29]. A numerical study on the catalytic combustion of H_2/air in a planar micro combustor conducted by Lu et al. [30] showed that there are three stages in heterogeneous reaction depending on the relative intensity of heterogeneous and homogeneous reaction, while homogeneous reaction played the main role in catalytic combustion, and the existence of heterogeneous reaction can decrease the yield of byproduct and improve the fuel conversion completeness. By changing the ratio of the catalytically-active area to the geometrical channel surface area, Pizza et al. [22] obtained the flame stability diagrams of oscillating, asymmetric, and symmetric V-shaped flames in a planar channel of 1 mm height with Pt-coated walls under different inlet velocities and catalytic reactivities. Flame stability and heat transfer of methane/air mixtures in catalytic micro combustors was numerically investigated by Chen et al. [31].

Although the catalytic combustion was concerned in micro combustion field, it is still not clear in the understanding of the chemical interaction mechanism while the published work mainly focused on the interaction mechanism of hydrogen combustion, and the combustion overall characteristics, such as the stable limits, the combustion efficiency and so on. Exploring the chemical interaction mechanism in the catalytic combustion of methane can give guide to the practical use of catalytic combustion in microscale and control of the combustion intensity through catalyst. In this work, numerical investigation of catalytic combustion of methane/air mixture in varies channels is carried out to illuminate the characteristics of heterogeneous reaction and its effect on homogeneous reaction. Chemical analysis, involving the consumption and production of main species, such as CH_4, O_2, CO, CO_2, and H_2O by homogeneous and heterogeneous reaction is discussed in detail to acquire the chemical interaction mechanism between heterogeneous and homogeneous reaction.

2. Numerical models and simulation approach

2.1. Computing model and boundary conditions

The schematic diagram of the micro channel is shown in Fig. 1 with length (l) of 15 mm and wall thickness (δ) of 0.5 mm. Simulations in the channels whose width (d) varying were conducted to analysis the scale effect in catalytic combustion. 316 stainless steel was selected as the wall material, and the inner surfaces of micro channel were covered with Pt foils with a surface site density of 2.72×10^{-8} kmol/m^2.

Using the commercial CFD code FLUENT [32], the mass, momentum, energy, and heat transfer was simulated in a two-dimensional (2D) simulation model. Knudsen number was less than the critical value of 0.001 in these cases. Thus, the continuous model and no-slip conditions were appropriate, and the Navier–Stokes equations were still applicable. The laminar model was used because of the low Reynolds number (Re = 33.08 in the channel of d = 2.80 mm based on a velocity of 0.3491 m/s). A first-order up-wind scheme is used to discretize the convective terms in steady mass, momentum, energy and species equations while a second-order central differencing schemes is utilized to discretize the diffusion terms. The pressure-velocity coupling is treated using SIMPLE algorithm. The specific heat of species was calculated using a piecewise polynomial fitting method. The specific heat of the mixture was calculated using the mixing law, and the mixture gas density was calculated using the ideal gas law. The thermal conductivity and viscosity were calculated as a mass-fraction-weighted average of all species, and the kinetic theory was selected for the mass