

Recent Advances and Challenges in the Catalytic Combustion at Micro-Scales

Junjie Chen, Deguang Xu

Abstract—The high energy density of hydrocarbon fuels creates a great opportunity to develop catalytic combustion based micro-power generation systems to meet increasing demands for micro-scale devices. In this work, the recent technological development progress in fundamental understanding of the catalytic combustion at micro-scales are reviewed. The underlying fundamental mechanisms, flame stability, hetero-homogeneous interaction, catalytic ignition, and catalytic reforming are reviewed in catalytic micro-scale combustion systems. Catalytic combustion and its design, diagnosis, and modeling operation are highlighted for micro-combustion application purpose; these fundamental aspects are reviewed. Finally, an overview of future studies is made. The primary objective of this review is to present an overview of the development of micro-power generators by focusing on the advances and challenges in the fundamental understanding of the catalytic combustion at micro-scales.

Keywords—Micro-combustion, catalytic combustion, flame stability, hetero-homogeneous interaction, catalytic ignition, catalytic reforming.

I. INTRODUCTION

MICRO-COMBUSTORS are emerging as a powerful tool for portable production of energy. Due to the large energy density of hydrocarbons, micro-combustion may eventually replace expensive and environmentally non-benign lithium batteries in cellular phones, laptops, and other communication devices [1]. In addition, due to the inherently higher heat-transfer coefficients of micro-scale systems, lower combustion temperatures may be envisioned, which can considerably minimize thermal nitrogen oxides formation. For the same reason, micro-combustors can be efficient heat sources for endothermic reactions, such as ammonia decomposition and steam reforming, in integrated micro-chemical systems for the production of hydrogen for fuel cell applications [2].

Despite the feasibility of pure homogeneous combustion at the micro-scale, the large surface-to-volume ratios of micro-combustors call for catalytic combustion [3]. Furthermore, although the use of catalysis offers versatility to promote chemical reactions in various industrial purposes, catalytic combustion has not been a majority of them since thermal runaway is hard to control in ordinary large scale applications. In micro-scale applications, however, the above weakness can be turned into one of the significant advantages for sustaining stable exothermic reactions with other

advantages, such as clean emission, moderate reaction temperature, no quenching distance and immobile heat release region [4].

Catalyst is generally utilized to resist the thermal quench, cope with the toxic gas emissions, extend flammability, and enhance the combustion stability [5]. In particular, catalytically combustion is suited for low-calorific value fuels because of the enhanced combustion stability at moderate reaction temperatures [6]. The concept of catalytically stabilized thermal combustion is to achieve fractional fuel conversion in catalytic micro-combustors, and in turn the remaining fuel is combusted in an ensuing homogeneous burnout region [7]. Application of combined hetero-/homogeneous combustion has been demonstrated to suppress most of the intrinsic flame instabilities appearing in air-fired combustion. Therefore, utilization of catalytic combustion provides an alternative solution for improving low flammability and combustion instability [8].

This review is primarily focused on numerical and experimental works that have been carried out with regard to catalytic micro-combustors. The review covers the flame stability, hetero-homogeneous interaction, catalytic ignition, and catalytic reforming. In addition, some fundamental aspects of catalytic combustion, modeling operation, design, and diagnosis are reviewed.

II. FLAME STABILITY

Flammability limit, ignition and extinction behavior are typical fundamental subjects of combustion science. Being associated with those subjects, the extinction limits and temperature characteristics of self-sustaining catalytic combustion were investigated in heat-recirculating combustors by [9]. In the experiments, a wide range of Reynolds numbers were tested using propane-air mixtures. Fig. 1 shows the extinction limits for a three-decade range of Reynolds numbers, channel width, and gas kinematic viscosity at ambient conditions. Notable feature is very wide self-sustained boundary of catalytic combustion, which has reached down to very small Reynolds numbers close to unity, being unsymmetrical to the stoichiometric condition. For higher Reynolds numbers, where both homogeneous and catalytic combustion could occur, catalytic limits were slightly broader but had much lower limit temperatures. At sufficiently high Reynolds numbers, homogeneous and catalytic limits merged. It is concluded that combustion at low Reynolds numbers in heat-recirculating combustors greatly benefits from catalytic combustion with the proper choice of mixtures that are different from those preferred for homogeneous combustion.

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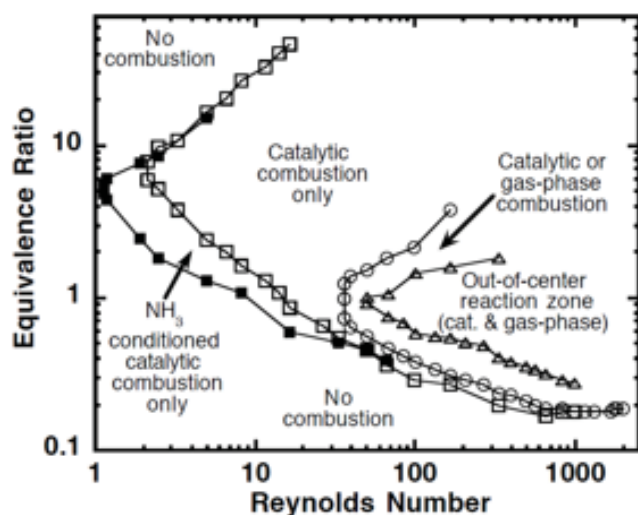


Fig. 1 Extinction limit map for gas-phase and catalytic combustion in Swiss roll combustors

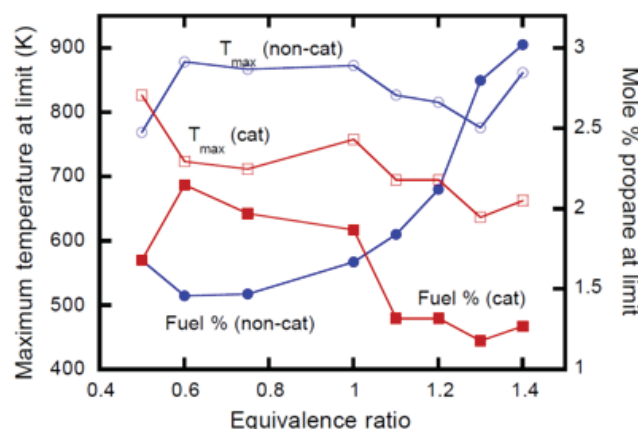


Fig. 2 Experimental values of minimum propane concentration in propane-oxygen-nitrogen mixtures supporting combustion in catalytic micro-channels as a function of equivalence ratio and corresponding maximum temperatures at these propane concentrations

In fact, low temperature self-sustaining catalytic combustion at the rich side of stoichiometry has been reported earlier by using a simple catalytic micro-channel [10]. Fig. 2 shows the experimental values of minimum propane concentration in propane-oxygen-nitrogen mixtures supporting combustion in catalytic micro-channels as a function of equivalence ratio and corresponding maximum temperatures at these propane concentrations. The limits to self-sustaining catalytic combustion were studied computationally using computational fluid dynamics. When the wall boundary condition was adiabatic, the equivalence ratio at the extinction limit monotonically decreased with increasing Reynolds numbers. In contrast, for non-adiabatic conditions, the extinction curve exhibited U-shaped dual limit behavior, that is, the extinction limits increased/decreased with decreasing Reynolds numbers in smaller/larger Reynolds numbers regions, respectively. The former extinction limit is caused by heat loss through the wall, and the latter is a blow-off-type extinction because of insufficient residence time, compared to the chemical

timescale. These heat-losses and blow-off-type extinction limits are characterized by small/large surface coverage of Pt(s) and conversely large/small numbers of surface coverage of O(s).

Karagiannidis et al. [11] numerically investigated the flame stability of lean methane-air and propane-air mixtures in platinum-coated, plane channel-flow catalytic microreactors. Stability limits were assessed as a function of inlet velocity, fuel type, and imposed external heat losses. Parametric studies were performed with a full-elliptic, two-dimensional numerical model employing elementary homogeneous reaction schemes for both fuels, a detailed heterogeneous reaction scheme for methane and a recently developed global reaction step for the oxidation of propane over platinum. They found that the higher diffusive transport of methane is critical in maintaining wider high inlet velocity stability limits (blowout) compared to those of propane, despite the higher homogeneous and catalytic reactivity of the latter. On the other hand, at the low velocity limits (extinction), propane exhibits a wider stability envelope. Homogeneous chemistry has a strong impact on the blowout limits. For the same mass throughput, smaller channel heights tolerate higher heat losses at the extinction branch of the combustion stability envelope due to the increased transverse fuel transport, while at the same time they exhibit narrower limits at the blowout stability branch because of the insufficient residence times at higher inlet velocities. Sui et al. [12] experimentally and numerically investigated the flame stability and heat transfer characteristics of a hydrogen-fueled microreactor. They found that higher mass throughputs reduce the surface temperature spatial non-uniformities, while the onset of homogeneous combustion lowers the catalyst surface temperatures and is thus detrimental for power generation applications. Comparisons of measurements and predictions are very favorable in terms of temperature probability density function (PDF) shapes and higher distribution moments. Counter-flow configurations yield narrower PDFs slightly skewed to the low temperatures, while the co-flow configuration yields mostly bimodal shapes. Radiation efficiencies increase with increasing equivalence ratio and inlet velocity. Application of the microreactor to power generation systems, in conjunction with thermoelectric devices, appears quite promising given the attained good spatial uniformity and the high values of surface temperatures.

III. HETERO-HOMOGENEOUS INTERACTION

Hetero-homogeneous interaction between gas-phase and surface reactions is also relevant to operation boundary of catalytic reaction. Although general stability characteristics including interaction and/or transition between them have not been fully elucidated, this subject has been addressed by several studies for macro-scale applications of nitrogen oxides reduction and catalytic partial oxidation [13]. Schwiedernoch et al. [14] showed that inclusion of homogeneous reaction modeling is required for capturing reaction of a mixture close to stoichiometry while heterogeneous reaction modeling alone is enough to reproduce phenomena for fuel lean methane-air mixture in a macro-scale honeycomb monolith catalytic

reactor. Norton et al. [15] fabricated single-channel catalytic micro-combustors and found that self-ignition, homogeneous combustion in parallel with catalytic combustion and audible “whistle” together with temperature bifurcation for hydrogen-air mixture. Experimental data for the oxidation of hydrogen/air mixtures over platinum/alumina micro-channels of different channel gap distances was presented. The role of gap distance in enhancing transport rates and changing the dominant chemistry was experimentally demonstrated. Spatially resolved temperature profiles indicate significant longitudinal non-uniformity. Finally, catalytic and homogeneous micro-combustors were briefly contrasted.

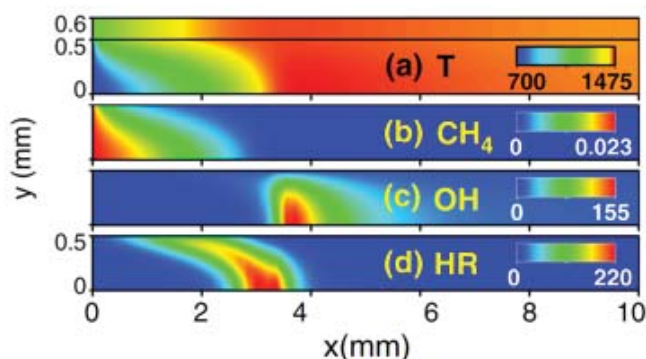


Fig. 3 Two-dimensional distributions of temperature, methane and OH mass fractions, and homogeneous heat release

Karagiannidis et al. [16] numerically investigated the hetero-/homogeneous steady combustion and the stability limits in methane-fueled catalytic microreactors (platinum-coated) at atmospheric pressure and high pressures to investigate the interplay of hetero-/homogeneous combustion, transport, and heat transfer mechanisms in the microreactor and to delineate combustion stability maps in terms of the underlying parameters. Simulations were carried out with a two-dimensional full-elliptic model for both the gas- and solid-phases. Elementary hetero-/homogeneous chemical reaction schemes were included along with heat conduction in the walls, surface radiation heat transfer, and external heat losses. Fig. 3 shows the two-dimensional distributions of temperature, methane and OH mass fractions, and homogeneous heat release. They found that homogeneous chemistry extended the low-velocity stability limits because of the establishment of strong flames and to an even greater degree the high-velocity blowout limits because of the heat release originating primarily from the incomplete homogeneous oxidation of methane. When considering the same mass throughput, the stable combustion envelope at high pressures is substantially wider than its atmospheric pressure counterpart because of the increased reactivity of both catalytic and homogeneous pathways at elevated pressures. Stable combustion could be sustained with extremely low solid thermal conductivities, while the stability limits reached their larger extent between 20 and 50 W/m·K, a range that covers many practical metallic compounds. The stability limits of catalytic microreactors are wider than those reported for

non-catalytic systems. Surface radiation heat transfer greatly impacts the energy balance and flame stability. At conditions well-below the flame stability limits, surface radiation provides an efficient heat loss mechanism that moderates the surface temperatures, whereas close to the limits it could stabilize combustion by transferring heat from the hotter rear of the channel to the colder front.

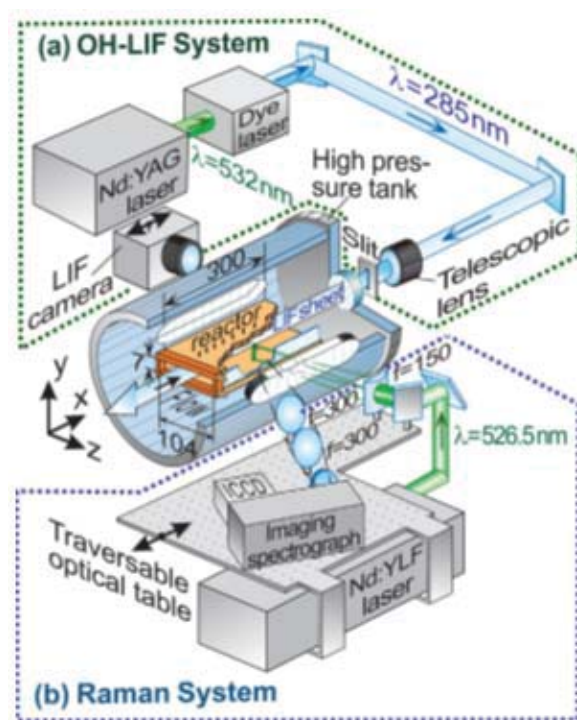


Fig. 4 Optical setups for the two-dimensional OH-LIF and the Raman measurements. All distances and focal lengths are in mm

Another computational study reported phenomena with similar tendencies containing hetero-homogeneous interaction for hydrogen and carbon monoxide oxidation over platinum. Zheng et al. [17] experimentally and numerically investigated the heterogeneous chemistry coupling of hydrogen and carbon monoxide over platinum for hydrogen/carbon monoxide/oxygen/nitrogen mixtures with overall lean equivalence ratios $\phi = 0.13-0.26$ and a pressure of 5 bar. Experiments were performed in an optically accessible channel-flow reactor at surface temperatures 510-827 K and involved in situ Raman measurements of major homogeneous species concentrations and thermocouple measurements of surface temperatures. Fig. 4 shows the optical setups and their positioning with respect to the reactor. They found that measured and predicted transition temperatures below which hydrogen inhibited carbon monoxide oxidation agreed well with each other, showing a main dependence on the overall equivalence ratio and a weaker dependence on the hydrogen: carbon monoxide ratio. Furthermore, this inhibition is non-monotonically dependent on the hydrogen: carbon monoxide ratio. This inhibiting kinetic effect of hydrogen is an outcome of the competition between hydrogen and carbon monoxide/oxygen for surface adsorption and, most

importantly, of the competition between the adsorbed H(s) and CO(s) for surface-deficient O(s). Transient simulations in practical catalytic channels revealed the interaction between thermal and kinetic effects. The effect of hydrogen: carbon monoxide molar ratio on the light-off times was quite strong, suggesting care when designing syngas catalytic reactors with varying compositions.

Badra and Masri [18] addressed the hetero-homogeneous interactions of different hydrocarbons over platinum in catalytic micro-combustors. Experiments are performed to study the effects of varying the incoming mixture temperature, equivalence ratio, and Reynolds number on the reactivity limits. Computational fluid dynamic calculations using detailed chemical kinetics are completed for a range of methane-air mixtures to resolve the impact of varying the incoming mixture temperature, equivalence ratio, and Reynolds number on the compositional structure of the flow. They found that the platinum plate temperature increases with increasing incoming mixture temperature and Reynolds number for flameless conditions. The reactive limits for compressed natural gas, propane and dimethyl ether are found to significantly broaden. The computed compositional structure confirmed the existence of a flame inhibition effect because of the presence of the catalyst. Stefanidis and Vlachos [19] developed the operation strategies for controlling the extent of homogeneous chemistry in catalytic reactors using a two-dimensional model for propane combustion over platinum in catalytic micro-combustors. They found that homogeneous chemistry is sustained for gaps well below the quenching diameter as a result of enhanced catalyst-induced heating. This finding has important ramifications for safety and catalyst lifetime, and could be used to produce chemicals, for example, in oxidative coupling and oxidative dehydrogenation reactions. The homogeneous chemistry contribution decreases with decreasing gap distance. Heterogeneous chemistry alone can occur under suitable compositions, flow rates, and heat loss/heat exchange rates. The synergism or competition between homogeneous and catalytic chemistries was also delineated.

IV. CATALYTIC IGNITION

Ignition or light-off of catalytic reaction is another key subject of catalytic combustion system. Aside from flame stability and safety requirements, micro-scale devices should also be fast starting, namely, the time required for warm-up from cold-start conditions should be short. This is also desirable in order to minimize emissions during start-up. Due to the large heat capacity of the reactor solid structure, such a device could have a long start-up time. A strategy of reducing the start-up time is to combust the unreacted hydrogen from the fuel cell anode off-gases to preheat the inlet stream. Hydrogen, which is self-igniting over platinum catalyst, can also be used to start-up hydrocarbon combustion.

As the vital role of detailed reaction modeling for understanding homogeneous combustion, detailed surface reaction modeling, coupled with transport at gas-surface interface, plays significant role for understanding catalytic ignition. Significant role of adsorption-desorption on catalytic

ignition was presented in the early numerical studies of Deutschmann et al. [20], though it was not addressed to the micro-power generation. They numerically studied the catalytic ignition of methane, hydrogen and carbon monoxide oxidation over platinum and palladium at atmospheric pressure. Two simple configurations are simulated: the stagnation flow field over a catalytically active foil and a chemical reactor with a catalytically active wire inside. The simulation includes detailed hetero-/homogeneous reaction mechanisms. The homogeneous transport and its coupling to the surface is described using a simplified multicomponent model. The catalyst is characterized by its temperature and its coverage by adsorbed species. The dependence of the ignition temperature on the fuel-oxygen ratio is computed and compared with experimental results. The ignition temperature of methane decreases with increasing methane-oxygen ratio, whereas the ignition temperature of hydrogen and carbon monoxide increases with increasing fuel-oxygen ratio. The kinetic data for adsorption and desorption are found to be critical for the catalytic ignition process. They determine the dependence of the catalytic ignition temperature on the fuel-oxygen ratio. A sensitivity analysis results in the rate-determining steps of the surface reaction mechanism. The bistable ignition behavior observed experimentally for lean hydrogen-oxygen mixtures over palladium is numerically reproduced. The abrupt transition from a kinetically controlled system before catalytic ignition to one controlled by mass transport after catalytic ignition is described by the time-dependent codes applied. Zheng et al. [21] investigated the homogeneous ignition of fuel-lean syngas mixtures over platinum at preheats and elevated pressures. They found that homogeneous oxidation is suppressed at atmospheric pressure because of the intrinsic slow homogeneous ignition kinetics in conjunction with the competition from the catalytic pathway for hydrogen and carbon monoxide consumption. The catalytically produced water has a strong kinetic impact on homogeneous combustion by inhibiting the homogeneous oxidation of both hydrogen and carbon monoxide at high hydrogen: carbon monoxide ratios and by promoting carbon monoxide homogeneous oxidation at low hydrogen: carbon monoxide ratios. The catalytically produced carbon dioxide always inhibited kinetically the homogeneous combustion of hydrogen and carbon monoxide, although its effect is much weaker compared to that of water.

Schultze et al. [22] numerically and experimentally investigated the hetero-/homogeneous combustion of syngas mixtures over platinum at fuel-rich stoichiometry to examine the impact of pressure, equivalence ratio and hydrogen: carbon monoxide volumetric ratio on homogeneous ignition and on the underlying catalytic processes. Experiments were performed in an optically accessible, platinum-coated, channel-flow reactor. The onset of homogeneous ignition was monitored with planar laser induced fluorescence of the OH radical at pressures up to 5 bar and with oxygen-LIF at higher pressures. The catalytic processes preceding homogeneous ignition were assessed with Raman measurements of major homogeneous species concentrations. Fig. 5 shows the comparisons between LIF-measured and predicted OH or oxygen distributions. They

found that catalytic reaction has a large sensitivity on homogeneous ignition. Adsorption of H radical significantly inhibited homogeneous ignition. Moreover, the key surface reactions affecting homogeneous combustion were the same for all pressures. For a given stoichiometry, homogeneous ignition was modestly dependent on the inlet monoxide ratio concentration because of the preferential catalytic oxidation of monoxide ratio that in turn increased the hydrogen: carbon monoxide ratio along the homogeneous induction region. Brambilla et al. [23] numerically and experimentally investigated the premixed syngas combustion dynamics in mesoscale channels with controlled wall temperature profiles. Simulations were carried out with a transient two-dimensional code, which included an elementary syngas reaction mechanism and detailed species transport. Simulations of the oscillatory flames, which appears in the form of ignition/extinction events of varying spatial extents, are very sensitive to the specific boundary conditions and reproduces qualitatively the flame topology, the ignition sequence (including the periodic reversion from upper-asymmetric to lower-asymmetric flame propagation), and the range of measured oscillation frequencies.

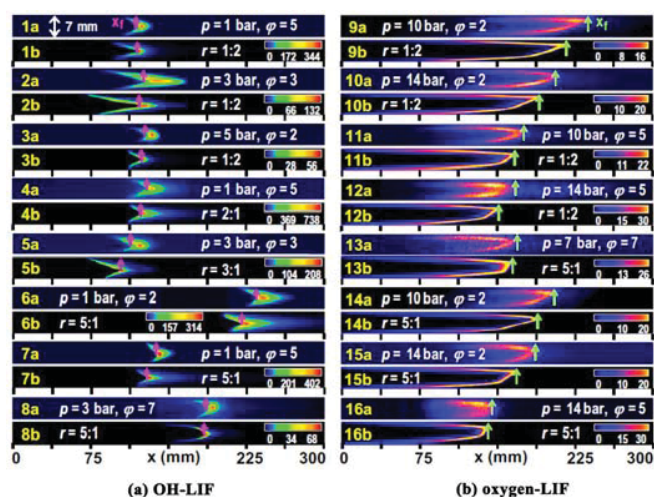


Fig. 5 LIF-measurements and simulations. Color bars provide predicted OH and hot oxygen (ppmv). Vertical arrows indicate flame positions

The self-ignition nature of hydrogen-air mixtures in catalytic micro-combustors offers an opportunity to self-ignite hydrocarbons. This concept may be a way toward elimination of ignition sources from micro-scale devices leading to further reduction of system size. Furthermore, since hydrogen is a main target for fuel cell applications, one can envision storage of small amounts of hydrogen during device operation from reforming of hydrocarbons that is subsequently used for startup. Deutschmann et al. [24] experimentally and numerically investigated the hydrogen-assisted catalytic ignition of methane over platinum at atmospheric pressure. They found the catalytic ignition is primarily determined by the catalyst temperature that is a result of the heat release because of catalytic hydrogen oxidation. Increasing hydrogen addition

ensures catalytic ignition, decreasing hydrogen addition requires an increasing methane feed for catalytic ignition. Based on this method, Norton and Vlachos [25] experimentally investigated the hydrogen assisted self-ignition of propane-air mixtures in catalytic micro-combustors. They described the transient and steady state behavior of these systems, and discussed the minimization of hydrogen usage and startup time. Experimental results shown that propane kinetically inhibits hydrogen catalytic combustion at low hydrogen fractions; the minimum hydrogen composition for self-ignition of propane-air mixture compositions is found to be relatively constant, irrespective of propane composition. Seshadri and Kaisare [26] presented a thorough numerical investigation of hydrogen self-ignition and hydrogen-assisted ignition of propane in catalytic micro-combustors from ambient cold-start conditions. They found that the hydrogen-assisted ignition is equivalent to selectively preheating the inlet section of the micro-combustor; the time to reach steady state is lower at higher equivalence ratio, lower wall thermal conductivity, and higher inlet velocity for both the ignition modes. Zhong and Yang [27] experimentally studied the hydrogen-assisted catalytic ignition characteristics of n-butane in a platinum-coated monolith catalytic reactor, and the chemical effect of hydrogen in hydrogen-assisted catalytic ignition of n-butane-air mixtures. They found that hydrogen has a positive chemical effect on hydrogen-assisted ignition and high hydrogen mole fraction is favorable to hydrogen-assisted ignition; the co-feed method and thermal insulation are beneficial to hydrogen-assisted ignition. Zimont [28] theoretically studied the self-ignition and quenching limits in catalytic micro-combustors and their sensitivity analysis to investigate the effect of the variations of geometrical, chemical and regime parameters on the boundary of the operating regimes. Agreement was found between the theoretical and experimental results reported by Barbato et al. [29]. Analytical method for prediction of the self-ignition and quenching limits was made. Sensitivity analysis of the combustion limits of the catalytic micro-combustor was carried out. Wu et al. [30] presented an experimental study on the self-ignition of hydrogen under different oxidation conditions and to explore how hydrogen assists carbon monoxide oxidation in a carbon dioxide-diluted stoichiometric stream via a catalytic reactor filled with catalyst. They found that the conversion ratio decreases as the volume fraction of hydrogen in the reactant mixtures increases in the cases of hydrogen oxidation with inert-diluted stoichiometric oxygen.

More practical approach is conducted to identify the effective ignition strategies for simple catalytic channel with heat conducting wall. Karagiannidis and Mantzaras [31] numerically investigated the start-up of methane-fueled, catalytic microreactors under conditions pertinent to microturbine-based power generation devices, and performed the transient simulations in plane-channel, methane-fueled microreactors made of either cordierite or FeCr alloy walls and coated with platinum catalysts. Detailed homogeneous and heterogeneous reaction mechanisms for the total oxidation of methane over platinum were used to investigate the ignition

characteristics for microreactors of a nominal geometry by independently varying the inlet mixture velocity, fuel-to-air air equivalence ratio, pressure, radiation properties of the solid, and reactor wall material (including wall heat capacity and thermal conductivity), and to assess the impact of the above parameters on the elapsed times required for reactor ignition and subsequent attainment of steady state. Fig. 6 shows the two-dimensional distributions of methane and OH radical mass fractions and of homogeneous temperature at four time instances, including ignition and steady state. They found that reactors with low wall thermal conductivity (cordierite material) exhibited shorter ignition times compared to higher thermal conductivity ones (FeCr alloy) because of the creation of spatially localized hot spots that promoted catalytic ignition. At the same time, the ceramic material required shorter times to reach steady-state. Higher inlet velocities reduced the time required for steady-state, however, at the cost of increased cumulative reactor emissions. Surface radiation heat transfer played a key dual role in the start-up process of low thermal conductivity channels. Radiation increased ignition times by removing heat away from the initial hot spot, but from the other side it decreased steady-state times because of a very efficient

transfer of heat from the rear to the front of the reactor. Homogeneous chemistry elongated the steady-state times for both ceramic and metallic materials and impacted the emissions of catalytic microreactors. Kaisare et al. [32] compared three ignition strategies for catalytic micro-combustors: heating the inlet feed above its ignition temperature, resistive heating using electric power, and spatially distributed (stratified) resistive heating. They found that, depending on velocity, wall conductivity, and power supplied (for resistive heating) or inlet temperature (for preheated feed), the fuel lights off either at the entrance (front-end ignition), towards the exit (back-end ignition) or in the middle of the reactor. The cumulative propane emissions are the highest for resistive heating of catalytic micro-combustors. Promoting front-end ignition, via locally heating the initial section of the reactor or by feed preheating, significantly reduces the ignition time and the emissions. Lower conductivity materials show shorter ignition times and lower emissions for all start-up modes. The time to steady state depends on start-up mode and wall conductivity. A good start-up strategy would be to ignite the catalytic micro-combustor with a low flow rate and then increase it.

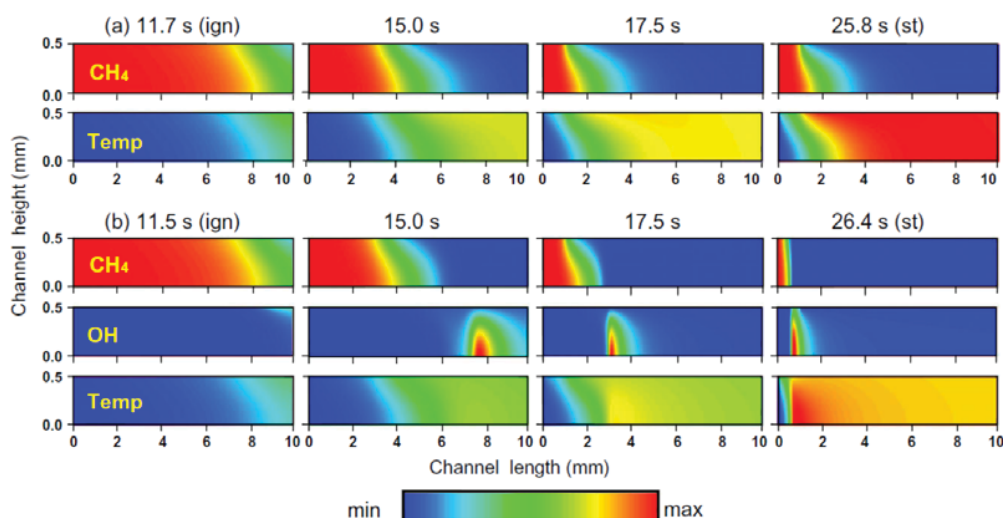


Fig. 6 Two-dimensional distributions of methane and OH radical mass fractions and of homogeneous temperature at four time instances, including ignition and steady state

V. CATALYTIC REFORMING

Hydrogen assisted catalytic combustion has been used in the catalytic combustors of gas turbines because of its low ignition temperature. Catalytic combustion of hydrogen normally occurs at room temperature and that of hydrocarbon occurs at elevated temperatures. Hydrogen addition not only decreases ignition temperature, but also reduces nitrogen oxide emission. Hydrogen assisted catalytic combustion is also used in portable catalytic micro-combustors. Furthermore, it can be used in a steam reforming reactor for hydrogen production [33]. When hydrogen is used as fuel for catalytic combustion in steam reforming reactors, neither preheating devices nor preheating energy is required, unlike in hydrocarbon combustions.

The catalytic combustor operates without additional

hydrogen, once ignited by hydrogen. However, most steam reforming reactor used hydrogen only as a fuel of catalytic combustion. To reduce the energy consumption, the minimum amount of hydrogen should be used by shutting off the hydrogen supply after start-up [34]. The steam reforming reactor should be investigated for various geometric flow configurations such as co-flow and counter-flow because the heat transfer characteristics of co-flow and counter-flow reactors are completely different; the reaction regions overlap in a co-flow reactor, but reactant depletions occur in the opposite direction in a counter-flow reactor.

There are a number of reforming techniques available including steam reforming, partial oxidation and auto-thermal reforming. Steam reforming was selected for a micro methanol

reformer because of its high attainable hydrogen concentration in the reformat gas and the low reforming temperature [35]. The methanol steam reforming reaction consists of two overall reactions; one is a primary process in the steam reforming of methanol and the other is the methanol decomposition to produce carbon monoxide. Kim [36] presented the development of a micro methanol reformer for portable fuel cell applications. The micro reformer consists of a methanol steam reforming reactor, catalytic combustor, and heat exchanger. Fig. 7 shows the construction of the micro methanol reformer combined with a catalytic combustor. The mixture of methanol and water enters the steam reformer at the top, and hydrogen and carbon dioxide as the reforming products leave the reactor. The mixture of hydrogen and air flows into catalytic combustors at the bottom with a counter flow stream against the reforming stream. The heat generated from the catalytic combustion is transferred to the steam reformer through the heat exchanger layer to increase the surface area and the suspended membrane to enhance the heat transfer. The porous catalyst supports are inserted in the cavity made on the glass wafer. The performance of the micro methanol reformer combine with the catalytic combustor was measured at various test conditions and optimum operation condition was sought.

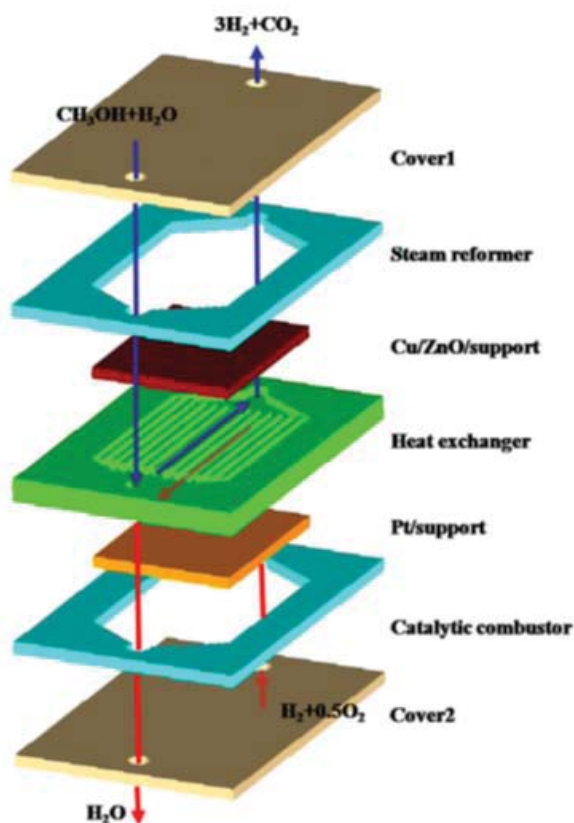


Fig. 7 The construction of the micro methanol reformer combined with a catalytic combustor

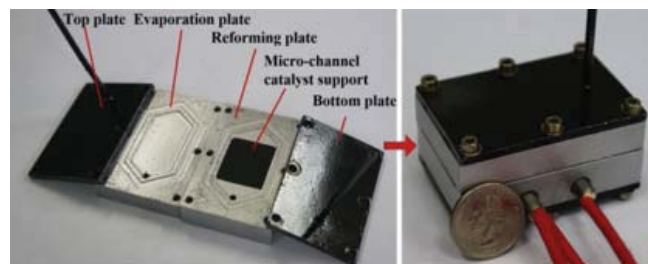


Fig. 8 The assembled micro-reactor embedded by micro-channel catalyst support coated with catalyst

Porous materials exhibit the advantages of large specific surface area and uniform coating of catalyst and have the potential to become a generation of catalyst support for hydrogen production. In reality, nickel foam, alumina foam and sintered copper fiber materials have already been applied as catalyst supports in various reactions [37]. To improve the energy conversion, Mei et al. [38] proposed an innovative micro-channel catalyst support with a micro-porous surface and fabricated using a layered powder sintering and dissolution method (LPSDM). The surface morphologies of the micro-channel catalyst support with a porous surface were characterized by scanning electron microscopy (SEM) and laser scanning confocal microscope, and an ultrasonic vibration test was carried out to analyze the adhesion strength of the catalyst. Subsequently, the coated micro-channel catalyst support was applied to hydrogen production via methanol steam reforming. The catalyst adhesion strength and methanol conversion by micro-channel catalyst support with a micro-porous surface were compared with the catalyst support with a non-porous surface. They found that the catalyst support with a micro-porous surface shows better catalyst adhesion and obvious advantages in hydrogen production rate and methanol conversion.

VI. FUTURE STUDIES

Some concept fundamentals attributed to nature of a small scale system, such as weak flame, specific instabilities/dynamics in micro-scale system, pattern formations, non-equilibrium effects, homogeneous and heterogeneous reaction interaction, are just on the horizon. Effects of wall/flame and thermal/chemical interactions play an important role because of the large surface/volume ratio. Exploration in other scaling issues in fluid dynamics, heat transfer, thermodynamics, and chemical reaction/combustion may result in fundamentals and developments. Studies on such nano-scale energetic materials are also collecting increasing attentions. By establishing well-defined experimental conditions, micro flow reactor with temperature gradient is started to be used for general ignition/combustion study by validating and examining the chemical kinetics for alternative fuels. Such trial was conducted using weak flames in a micro-channel with prescribed wall temperature profile. Since weak flames in a heated channel are on the ignition branch, ordinary multi-stage ignitions of given mixture are converted into the stabilized stationary multiple weak flames by the

methodology. Collaborations of micro-combustion studies with cutting-edge interdisciplinary study areas, such as nano-materials and bio-materials, visualization and diagnostics technologies are also encouraged since a variety of physical-chemical phenomena being observed in micro-scale systems can be further enriched by the synergetic effects.

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