



Effects of carbon dioxide in oxy-fuel atmosphere on catalytic combustion in a small-scale channel



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ABSTRACT

The effect of CO₂ dilution on oxy-fuel reaction over catalytic surface is experimentally investigated in a small-scale channel in terms of heat transfer, chemical reactivity as well as interplay between heterogeneous and homogeneous reaction. There are two kinds of small-scale reactors, tubular reactor and channel reactor, respectively, used in this study. In the tubular reactor, the interaction between heterogeneous and homogeneous reaction on tubular platinum reactor are addressed based on the resulting surface temperatures of the tube and fuel conversion ratios. CO₂ would absorb chemically-induced heat release of hydrogen, but in the meantime heat up the flowing mixture via radiative and convective heat transfer. In the channel reactor, the results demonstrate that the segmented catalyst with cavities has minimal oxygen concentration to hold catalytically stabilized thermal flame in a channel, and performs approximately complete fuel conversion. Besides, CO content in flue gas is increased in the case of segmented catalyst with cavities. It speculates that CO₂ decomposes CO through the reaction of CO₂+H=CO+OH in gas phase in the vicinity of the catalyst surface, and the requested H radical and thermal energy are provided by the neighboring heterogeneous reaction.

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1. Introduction

As the advent of industrial evolution, strong and correlated evidence elaborates that both the average global temperature and the atmospheric carbon oxide concentration have significantly increased. Technological solution to this problem is believed to rely heavily on a substantial improvement in energy conversion and utilization efficiencies, CCS (carbon capture and sequestration), and renewable sources such as biomass, hydro, solar, wind and geothermal energy. Accordingly, oxy-combustion integrating with CCS is considered as one of appropriate and practical approaches to timely curb the increasing CO₂ emission [1]. Oxy-fuel combustion is the technology for which instead of using air as oxidizer pure oxygen or a mixture of O₂ and recycled flue gas is used to generate high CO₂ concentration product gas to facilitate efficient carbon

capture [2]. In general, O₂ is provided from air separation unit and CO₂ is recirculated from flue gas with water removal. The oxidizer in oxy-fuel combustion usually consists of O₂ and CO₂. However, the apparent difference in the thermal and chemical properties of N₂ and CO₂ leads to significantly different combustion behavior for oxy-fuel from air-fuel combustions [3]. The thermal and physical properties of N₂ and CO₂ relevant to oxy-fuel combustion are summarized in Table 1. For heat transfer, radiative and convective heat transfer are significantly different between oxy-fuel and air-fuel combustion. Unlike N₂, a symmetric diatomic gas, the oxy-fuel flue gases, mainly consisting of triatomic gases of CO₂ and H₂O, have large emissivity and absorption coefficients due to their non-transparency to radiation. The absorption and radiation in oxy-combustion are stronger than those in conventional air-fuel combustion with identical gas temperatures. Andersson et al. [4,5] investigated the radiation intensity of propane-fired oxy-fuel flames, and pointed out that the gas radiation in oxy-fuel combustion is apparently higher. For convective heat transfer, Smart et al. [6] demonstrated that the contribution of convective heat transfer in oxy-combustion increased with increasing flue-gas recirculating ratios. For thermodynamic properties, although the specific heats of CO₂ and N₂ are similar on mass basis, the CO₂ heat

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Table 1

Comparison of selected thermal and physical properties of CO₂ and N₂ at 1 atm and 1000 K.

Thermal and physical property	CO ₂	N ₂
Density (kg/m ³)	0.5362	0.3413
Specific heat capacity (kJ/kgK)	1.2343	1.1674
Volumetric heat capacity (kJ/m ³ K)	0.662	0.398
Kinematic viscosity (m ² /s)	7.69e-5	1.2e-4
Thermal conductivity (W/mK)	7.057e-2	6.599e-2
Thermal diffusivity (m ² /s)	1.1e-4	1.7e-4
Mass diffusivity (m ² /s) ^a	9.8e-5	1.3e-4

^a Mass diffusivity refers to the binary diffusion of O₂ in CO₂ and N₂.

capacity on mole basis is 1.66 times higher than that of N₂ because of its larger molecular weight. Therefore, there is a significant reduction in the flame temperature for oxy-fuel combustion. In order to match the gas temperatures and heat transfer performances with that of air-fuel combustion, a wide range of O₂ contents in the oxidizer (23–35%) are needed for oxy-fuel combustion, especially for plant retrofits. Croiset et al. [7] demonstrated that in order to match the gas temperatures and heat fluxes of air-combustion conditions, O₂ mole fraction in oxy-fired conditions for bituminous and sub-bituminous coals should be raised to between 28% and 35%.

On the other hand, unlike N₂ in air-combustion, CO₂ plays an important role in oxy-fuel combustion due that CO₂ can actively participate in the combustion chemical reactions. High CO₂ concentration may affect the combustion characteristics through direct chemical reactions of CO₂, for instance, laminar flame speed, a fundamental parameter describing many features related to reactivity, diffusivity and exothermicity of the combustible mixtures. Oh and Noh [8] examined the flame speed of oxy-fuel mixtures at a fixed oxygen concentration for various equivalence ratios. The results are much lower than the flame speeds of air-fuel mixture at the same condition. Hu et al. [9] numerically investigated the effects of CO₂ dilution on flame structure and reaction pathway in oxy-fuel combustion. Several studies have reported that CO₂ is not an inert in oxy-fuel combustion, but actively participates in chemical reactions primarily through the reaction CO₂ + H = CO + OH [10,11]. According to aforementioned chemical reaction, the CO concentration in oxy-fuel combustion is generally found greater than that in air-fuel combustion [12,13].

The replacement of N₂ with CO₂, when switching to oxy-fuel combustion, would also narrow the flammability limits and induce combustion instability. In order to overcome the shortcomings associated with the operation of oxy-fuel combustion in retrofitted or tailored furnace, many approaches and strategies on operation processes are addressed recently, such as oxygen enrichment in the oxidizer [7], optimized flue gas recycle ratios [14], or gas stream preheating [15]. However, the capital and operating costs associated with pure oxygen supply is considerably high, so that the reduction of oxygen concentration in oxy-fuel combustion is regarded as a priori challenge to implement and disseminate the application of oxy-fuel technology in industry sectors.

Catalyst is generally utilized to resist the thermal quench, enhance the combustion stability, extend flammability of low-calorie fuel [16,17], or cope with the toxic gas emissions [18]. In particular, catalytically stabilized thermal combustion is suited for low-calorific value fuels due to the enhanced combustion stability at moderate reaction temperatures [19]. The concept of catalytically stabilized thermal combustion is to achieve fractional fuel conversion in a heterogeneous reactor, and in turn the remaining fuel is combusted in an ensuing homogeneous burnout zone. Application

of combined hetero-/homogeneous combustion has been demonstrated to suppress most of the intrinsic flame instabilities appearing in air-fired combustion [20]. Therefore, utilization of catalyst combustion in oxy-fuel combustion provides an alternative solution for improving low flammability and combustion instability in oxy-fuel combustion.

In this study, employing catalyst in the oxy-fuel environment is attempting to induce catalytically stabilized thermal combustion, namely the coexistence of heterogeneous and homogeneous reaction, with low oxygen concentration requirement in the oxidizer, and in the meantime to improve the narrow flammability and flame instability of oxy-combustion. However, there are some works discussing the effect of carbon dioxide addition or dilution in hydrogen or methane mixtures on catalyst reactivities and catalytic combustion [21,22], but limited papers for oxy-fuel environment [23]. Benedetto et al. discussed the effect of CO₂ addition (up to 30% in mixture content) on catalytic CH₄ combustion over a perovskite-based monolith at high pressure [22]. It indicated that the presence of CO₂ retards ignition and shifts the ignition pressure. In addition, once ignition has been attained, the catalytic surface temperature increases upon an increasing CO₂ content. Reinke et al. investigated the effect of flue gas dilution on the heterogeneous and homogeneous reaction of fuel-lean CH₄/O₂/N₂ mixture in experimental and numerical approaches [23]. The results illustrated that the addition of H₂O inhibits the catalytic methane conversion due to increasing OH radical occupying catalyst surface site, but the addition of CO₂ has no direct chemical impact on the catalytic pathway. However, the dilution of high CO₂ content in the mixture usually accompanied with a large amount of CO production. It is difficult to identify CO formation coming from the product gas of methane incomplete combustion or dissociation of CO₂ diluent gas in surface reaction or gas-phase reaction. In general, there are two kinds of catalysts extensively used in industry and transportation sectors, supported catalyst and metal catalyst (platinum and palladium), respectively. Supported catalyst is to coat or spray catalytic materials on ceramic substrates, such as honeycomb, mesh or bead. Meantime, honeycomb and tube are common and extensive configurations in catalyst applications. In order to simplify the experiment in this study, a tubular platinum tube and a ceramic catalytically-coated channel with various catalyst layouts are engaged to simulate a single catalytic channel of honeycomb in oxy-fuel environment and delineate the chemical reactivities of oxy-fuel over catalyst surface at conditions of broadly varying oxygen contents and flow throughputs.

2. Experimental apparatus

In this study, two different reaction sections are used to investigate the oxy-combustion phenomena in a catalytic channel. The first reaction section is a simple TP (tubular platinum) reactor, as shown in Fig. 1(a). The TP reactor consists of a 120 mm-long quartz tube (ID: 4 mm, OD: 6 mm) and 20 mm-long platinum tube (ID: 3 mm, OD: 4 mm). The platinum tube is positioned inside the quartz tube, and the distance between the inlets of the platinum tube and quartz tube is 40 mm. The second reaction section is a RCC (replaceable catalyst-channel) reactor with the dimension of 74 mm in length, 42 mm in width and 15 mm in height, as shown in Fig. 1(b). Two spark plugs are used for ignition in the reactor, and two slots are engaged to place in parallel ceramic sticks deployed with different catalyst layouts and configuration. The dimension of ceramic stick is 40 mm in length, 4 mm in width and 4 mm in height. The two ceramic sticks in parallel form a channel with the dimension of 60 mm in length, 4 mm in width and 4 mm in depth. The location of spark igniter is 5 mm from the inlet of the channel. Based on our previous studies [24–26], it indicates that varying

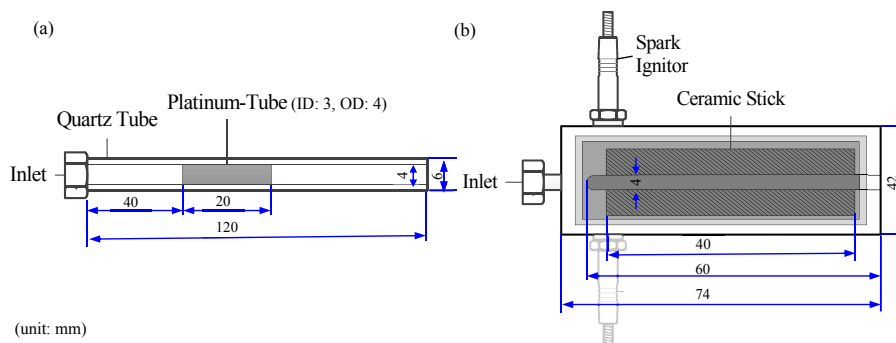


Fig. 1. Schematic diagram of (a) the tubular platinum-tube and (b) replaceable catalyst-channel reactor.

catalyst configurations and layouts are strongly related to the inception of catalytically stabilized flame, chemical reactivities, as well as optimal operation ranges. There are five types of channel surface disposition considered: straight channel, non-catalytic cavity channel, single catalytic channel, multi-segment catalytic channel, and multi-segment catalytic channel with cavities, respectively, as shown in Fig. 2. The total area of catalytic disposition is maintained constant for cases both with and without catalyst segmentation. The single catalytic channel has 14 mm-long catalytic surfaces on both lateral walls of the channel, while the segmented catalytic channel has 2 mm-long catalysts with seven segments on lateral walls. For the case of multi-segment catalyst with cavities the catalyst disposition consists of seven 2 mm-long-segments and seven cavities (2 mm (l) \times 4 mm (w) \times 1 mm (d)) in the channel. The catalyst contained in the reactor is a high-temperature platinum (Pt) catalyst typical of that used in catalytic combustion experiments. The substrate of the catalyst is made of alumina with washcoat surface. It has a desired low coefficient of thermal expansion, high temperature stability, good porosity and excellent oxidation resistance. The platinum molecules are coated on the washcoat surface with a density of 2.707×10^{-11} mol/mm².

The washcoat material is gamma alumina (γ -Al₂O₃) which has a high surface area and the maximum working temperature is about 1000 °C. The RCC reactor is covered by a lid with a quartz window for experimental observation.

Fig. 3 shows the experimental set-up for the two reaction systems. For identifying the catalytic and gas-phase reactivities of CO₂ in oxy-combustion, H₂ is used as fuel due to the simple product gas H₂O in flue gas. O₂, N₂ and CO₂ from pressurized bottles are metered by digital mass flow meters (Brooks 5850E) with 2% of uncertainty, and then mixed with H₂ in the premixing chamber. Regarding to the oxy-fuel experimental conditions, the oxygen concentration ranges from 22 to 30 vol.% in the oxidizer, and equivalence ratio for two reaction systems spans from 0.4 to 0.7. The premixing chamber is filled with beads and cross-flow grids to produce a well-premixed mixture with uniform velocity at the exit. The resulting O₂/N₂/H₂ or O₂/CO₂/H₂ reactant mixtures are injected into the reaction section. The reaction section is placed in a digital-control electric heater in order to counteract the external heat loss, and the surround temperature of the reaction chamber is fixed at 673 K, as shown in Fig. 3. The camera is used to observe the combustion phenomenon in the channel, and the 500 μ m beaded-sized

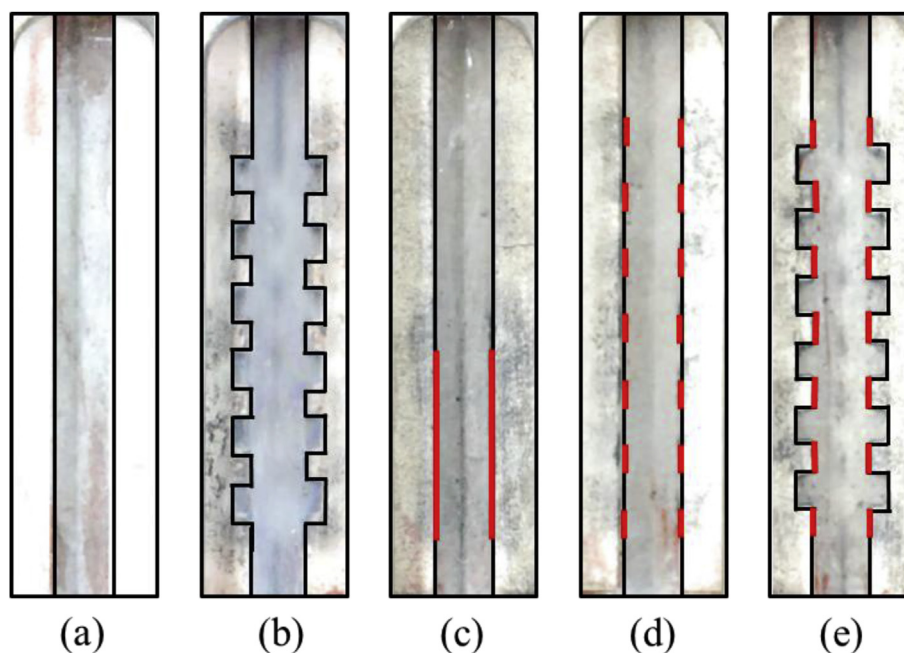


Fig. 2. Five different channel configurations in replaceable channel reactor, including (a) straight channel, (b) cavity channel, (c) single catalytic channel, (d) segmented catalytic channel, and (e) segmented catalytic channel with cavities, respectively.

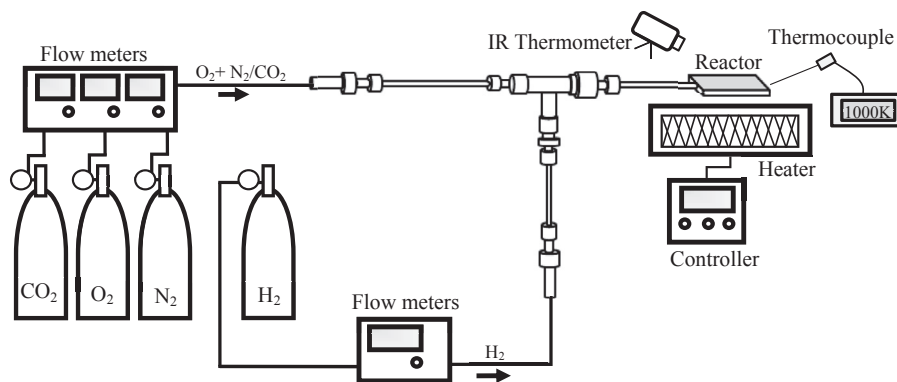


Fig. 3. Schematic diagram of the experimental setup.

R-type thermocouple is placed at the exit of the reactor to monitor the reaction. In our previous papers [26,27] the exit gas temperature is significantly different for the conditions of only heterogeneous reaction and the combination of hetero-/homo-geneous reaction. When the exit gaseous temperature is around or below 673 K, it means that there is only heterogeneous reaction occurrence in the reactor. The resulting heterogeneous reaction is difficult to heat up the flowing mixture due to short residence time and low conductivity, so that the gas temperature of flue gas is usually around or below 673 K. Similarly, when the exit gaseous temperature is higher than 1000 K, it means that the heterogeneous and homogeneous reaction is occurred in the reactor. Chemical exothermicity could release plentiful thermal energy in the gas phase, and it leads to increase flue gas temperature. If the exit gaseous temperature is fixed around room temperature, it means no chemical reaction inducing inside the channel. Consequently, an easy, quick, and reliable approach to determine the presence of homogeneous reaction inside the channel is to monitor the temperature of flue gas close to channel exit. This approach had been proven by comparing the experimental and numerical results in our previous papers [26,27]. In addition, the surface temperatures of TP reactor are measured by an infrared thermal thermometer (RAYMA2SCCFL) and the emissivity is referred to the emissivity table of materials and calibrated by the isothermal furnace [27].

Furthermore, the flue gas is collected by the sampling pump (Universal-PCXR4) with a needle probe. The 1 mm-diameter metallic needle probe is used to insert into the channel exit of the two reaction sections, so as to avoid the ambient air leaking in the sample bag and simultaneously reduce the temperature of flue gas by passing through the probe to meet the temperature tolerance of the sampling pump. The pumping speed of the sampling pump is set to 5 cc/min with minimum disturbance on flow structure of the reaction section. The captured flue gas is driven into a gas chromatography (GC, SHIMADZU GC-2014) for analyzing the gas components of the flue gas to determine hydrogen conversion ratio.

3. Results and discussion

3.1. TP (Tubular platinum) reactor

In order to explore the effect of oxy-fuel combustion over catalytic surface in the tubular reactor, non-catalytic metal tube (stainless steel) and catalytic metal tube (platinum) are operated in oxy-fuel environment at conditions of 0.4 equivalence ratio, 5 m/s total flow velocity and various oxygen concentrations from 21% to 30%. The experimental results show that the minimum oxygen concentration to sustain oxy-fuel combustion in a stainless steel tube is 25% in the oxidizer stream. When the oxygen content is

below 25%, the oxy-fuel flame will be subject to thermal quenching associated with wall and diluent gas effects. In the cases of oxygen contents ranging from 25% to 29%, the homogeneous reaction can stably anchor at the rear edge of the tube, near the tube exit, due to a small back-facing step between the metal tube and quartz tube, as shown in Fig. 4. The exposure time of the experimental photography is fixed at 0.1 s. By increasing oxygen concentration in the oxidizer stream, the rim of the tube is continuously heated up by the anchored flame until local incandescence, so that the mixture flowing through the tube is preheated via convective heat transfer. The hot spot of the tube provides a heat source for preheating and ignition of the flowing mixture. Therefore, the thermal recuperation mechanism between the flame and the metal tube is essential to stabilize homogeneous reaction in the tubular reactor. When the oxygen concentration is increased to 30% in the oxidizer, for instance, the flame temperature increases correspondingly due to the reduction of diluent gas that induces flame flashback, as seen in Fig. 4(e) a flame stabilized far-upstream near the tube entrance.

In general, the flame stabilization in a small-scale tubular reactor is based on the coupling between flow field and thermal interaction. However, the thermal balance among the flame, the non-catalytic metal tube and diluent gas is of significance on the stabilization of oxy-fuel flame in a small-scale tube. The thermal release of hydrogen oxidation is absorbed by the diluent CO_2 and metal tube, and scattered/convected to the ambience. The heated metal tube would partially recuperate the thermal energy to pre-heat the unburnt mixture flowing through the tube via convective heat transfer, and ultimately enhance the flame speed and flame stabilization. Enhanced flame speed is detrimental to stabilize air-fuel combustion in a small tube, and flame flashback may occur due to unbalanced mixture velocity and flame speed as well as the lack of flame stabilizer. Therefore, the thermal balance between the flame and the tube is important for small tube flame stabilization

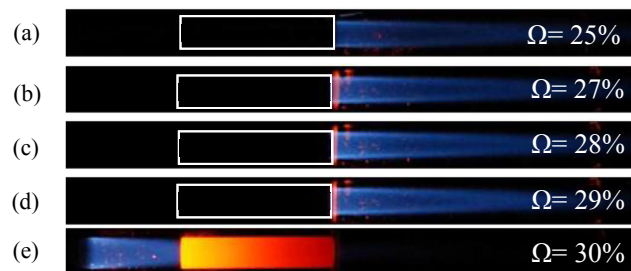


Fig. 4. The oxy-combustion phenomena in a stainless-steel-tube at $\Omega =$ (a) 25%, (b) 27%, (c) 28%, (d) 29% and (e) 30%, and fixed equivalence ratio = 0.4, total flow velocity = 5 m/s.

and subject to disturbance by increasing oxygen concentration in oxidizer stream and surface temperature.

Fig. 5 shows the experimental photography of hydrogen reaction in oxy-fuel condition at an equivalence ratio equal to 0.4, total flow velocity equal to 5 m/s and oxygen concentrations in oxidizer stream varying from 21% to 30%. The results reveal that the heterogeneous reaction can be sustained in oxy-fuel condition with various oxygen contents ranging from 21% to 24%. Owing to the inherently high sticking efficiency to platinum, hydrogen is prone to trigger heterogeneous reaction over platinum. The illumination intensity along the tube implies the location and distribution of heterogeneous reaction. The illumination intensity increases with increasing oxygen concentration. Compared with the non-catalytic stainless steel case, the existence of catalyst in the tubular reactor can extend the operation range of oxy-fuel reaction. The minimum oxygen concentration required for oxy-fuel reaction in the platinum tube can extend down to 21%. However, when oxygen content is raised to 25%, light bluish flame is found downstream of the hot bright tube. It is the catalytically stabilized homogeneous reaction, but the flame is unstable and pulsating. Once the oxygen content is increased to 26% and up, the catalytically stabilized flame can propagate upstream and stabilize at the leading edge of the tube. When the oxygen concentration ranges from 26% to 29% in the oxidizer stream, the combined hetero-/homogeneous reaction is presented in the platinum tube. It is noteworthy that the flame anchoring position can be seen apparently at the leading edge of the tube, especially in Fig. 5(g) and (h). Definitely, a competition for hydrogen, oxygen and radicals between heterogeneous and homogeneous reactions is anticipated. The catalytically stabilized thermal flame would primarily combust larger amount of hydrogen, and the remaining hydrogen would be consumed via heterogeneous reaction over the platinum tube. When the oxygen content increases to 29%, the homogeneous reaction would be accelerated and cause flame flashback, as shown in Fig. 5(i). Most

hydrogen is consumed in upstream homogeneous reaction and it leads to suppressing heterogeneous reaction by fuel competition, so as to weaken the incandescent intensity of the platinum tube.

Unlike the thermal recuperation mechanism in stainless steel case, the transport of heat from the hot wall to the flowing gas is less effective than the transport of hydrogen from the channel core toward the wall whereby inducing heterogeneous reaction. In order to further examine the interplay between heterogeneous and homogeneous reactions over the platinum tube, the surface temperatures along the tube and the residual hydrogen concentration in flue gas are monitored to clarify the effect of oxy-fuel environment on catalyst surface. Fig. 6 shows the measured surface temperature along the platinum-tube and Fig. 7 shows the hydrogen conversion ratio of the TP reactor at the condition of equivalence ratio = 0.4, total flow velocity = 5 m/s and various oxygen contents in oxidizer stream from 22% to 28% without the unstable case of 25%. In the cases of oxygen contents ranging from 22% to 24%, homogeneous ignition is suppressed by diluent gas (CO_2) with high heat capacity, but heterogeneous reaction overcomes the inhibition due to the diffusional imbalance of hydrogen and carbon dioxide and the relatively high sticking coefficient of hydrogen compared with that of carbon dioxide. Heterogeneous reaction becomes dominant in the hydrogen oxidation reaction in oxy-fuel environments for low oxygen contents. The surface temperatures along the tube increase with increasing oxygen contents in the oxidizer, as shown in Fig. 6. However, hydrogen conversion ratio for oxygen contents ranging from 22% to 24% are similar, even the fuel conversion ratio for the case of 24% O_2 in the oxidizer is slightly dropping, as shown in Fig. 7. It is anticipated that the increasing oxygen content is accompanied by decreasing carbon dioxide content in the oxidizer, so that the effect of diluent gas is reduced. In general, the surface temperature of catalyst required for O_2 desorption is higher than that for H_2 . Therefore, excessive oxygen occupies the active sites of the catalyst and inhibits the heterogeneous reaction of hydrogen over platinum. Nonetheless, the influence on suppression of heterogeneous reaction due to excessive oxygen is less than that on the reduction of heat loss through the absorption of diluent gas. Accordingly, the results demonstrate increasing surface temperature with slightly reduction on fuel conversion ratio in low oxygen contents cases.

In the case of 25% O_2 in the oxidizer, the inception of homogeneous reaction is initiated, but heterogeneous reaction inhibits

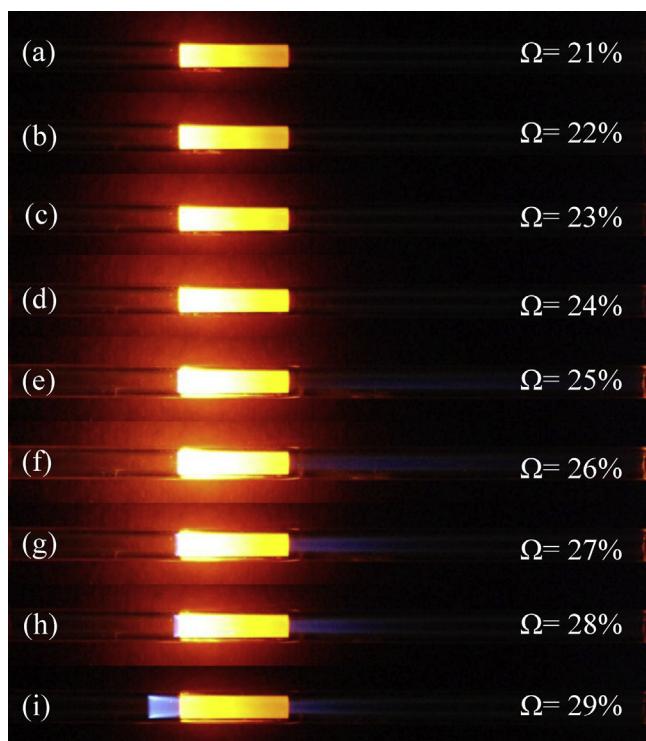


Fig. 5. The oxy-fuel reaction of tubular platinum reactor in various oxygen volumetric concentrations in oxidizer.

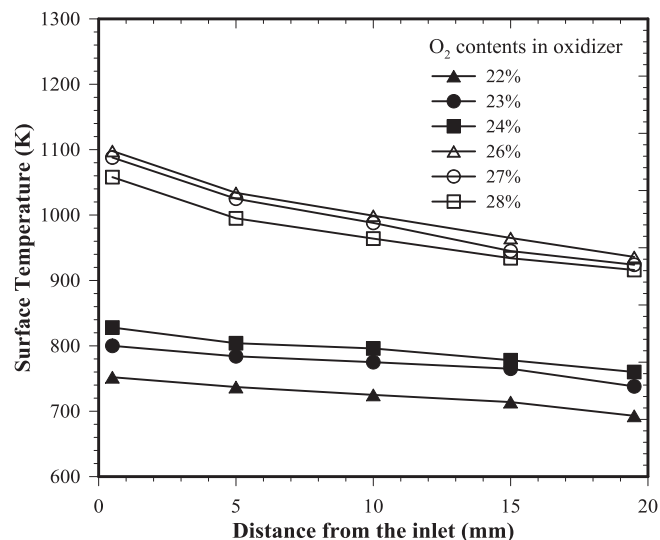


Fig. 6. Measured wall temperature along the tubular platinum at the condition of equivalence ratio = 0.4, total flow velocity = 5 m/s and various oxygen concentrations in oxidizer from 22 to 28%.

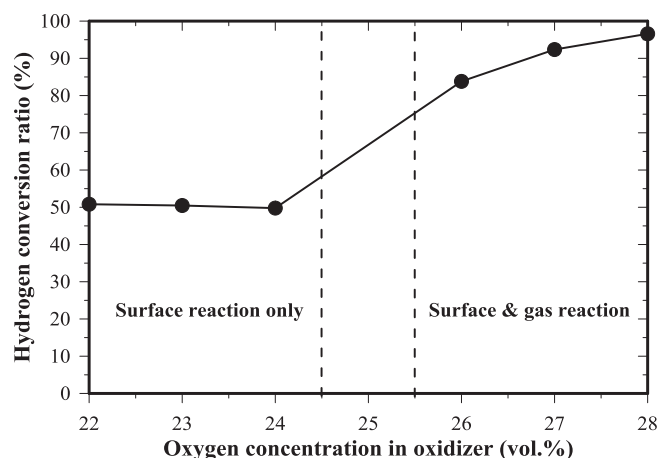


Fig. 7. The hydrogen conversion rate of tubular platinum reactor in various oxygen contents in oxidizer and fixed equivalence ratio = 0.4 and total flow velocity = 5 m/s.

homogeneous ignition mainly via competitive fuel depletion and radical quenching. Besides, the existence of carbon dioxide is detrimental to sustain homogeneous reaction due to thermal quenching effect. The factors delineated above give rise to reaction instability in the TP reactor. When oxygen content increases to 26%, it is significant to find the homogeneous reaction anchoring at the leading edge of the tube. The surface temperatures along the tube increase accordingly and hydrogen conversion ratio approaches to 85% at the tube exit. It is noteworthy that the surface temperatures along the tube decreases as oxygen content increases from 26% to 28% in the oxidizer, as shown in Fig. 6. Despite the tendency of surface temperature reduction depending upon the increasing oxygen content, the hydrogen conversion ratio is evidently increasing, especially approaching complete conversion for the case of 28% O_2 in the oxidizer. The effect of homogeneous reaction is enhanced, and the domination of hydrogen reaction switches to homogeneous reaction in the cases of relatively high oxygen contents. As most of the hydrogen is consumed in upstream homogeneous reaction, heterogeneous reaction becomes mild and the surface temperature of the tube is reduced.

In order to investigate the operational characteristics of the TP reactor, the above flame stabilization and reaction behaviors are summarized in terms of mixture flow velocity, three different flow velocities, 5, 7.5 and 10 m/s, and various oxygen contents in the oxidizer at a fixed equivalence ratio of 0.4 in Fig. 8. The flame stabilization and reaction behaviors can be categorized as heterogeneous reaction, combined heterogeneous and homogeneous reaction, unstable flame, and flame flashback. The results show that the different characteristic behaviors are mainly dependent on oxygen content in the oxidizer, except for the delayed flashback found in high flow velocity 10 m/s case. The plot also indicates the importance of the switch of flame/reaction characteristics at the inception of combustion instability as oxygen content is increased to 25%. It is believed that combustion instability is induced by the competition for fuel and radicals between heterogeneous surface and homogeneous gas phase reactions. The catalytically supported homogeneous reaction can sustain in oxygen contents ranging from 26% to 28% for all flow velocity cases. Oxygen content larger than 29% would cause flame flashback except of the case of flow velocity equal to 10 m/s. The range of catalytically supported homogeneous reaction can extend to oxygen contents equal to 29%.

In order to examine the effect of equivalence ratio on oxy-fuel reaction in various oxygen contents, the operating range of four equivalence ratios against various oxygen contents are addressed and shown in Fig. 9. The experimental results show that the case of

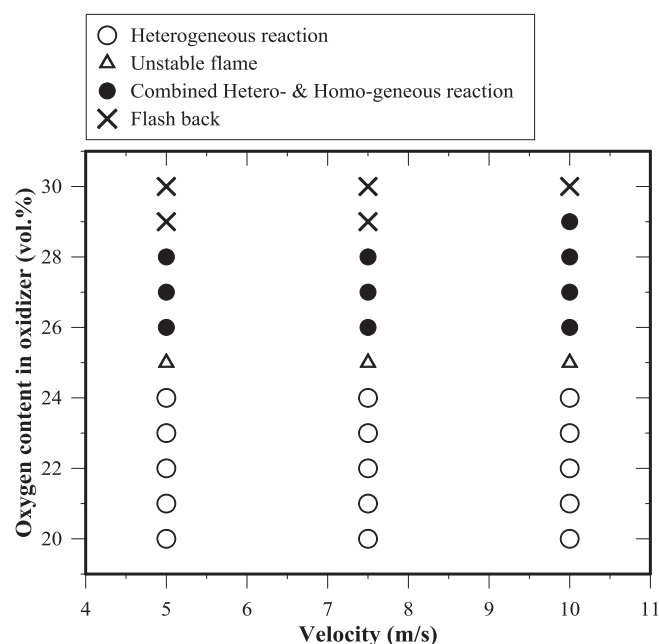


Fig. 8. The operating range of TP reactor for various flow velocity and oxygen content in the oxidizer in the condition of fixed equivalence ratio equal to 0.4.

equivalence ratio equal to 0.4 consists of four reaction behaviors in various oxygen contents, but the reaction behaviors only have heterogeneous reaction and flame flashback as equivalence ratio is increased to 0.7. It shows that the range of catalytically supported homogeneous reaction decreases when the equivalence ratio increases. It is noted that for lean flames increasing fuel concentration would enhance thermal heat release and accelerate flame speed, and eventually lead to early flame flashback due to the lack of proper flame flashback trap mechanism in the tube. Therefore, appropriate fuel content and flashback prevention mechanism are

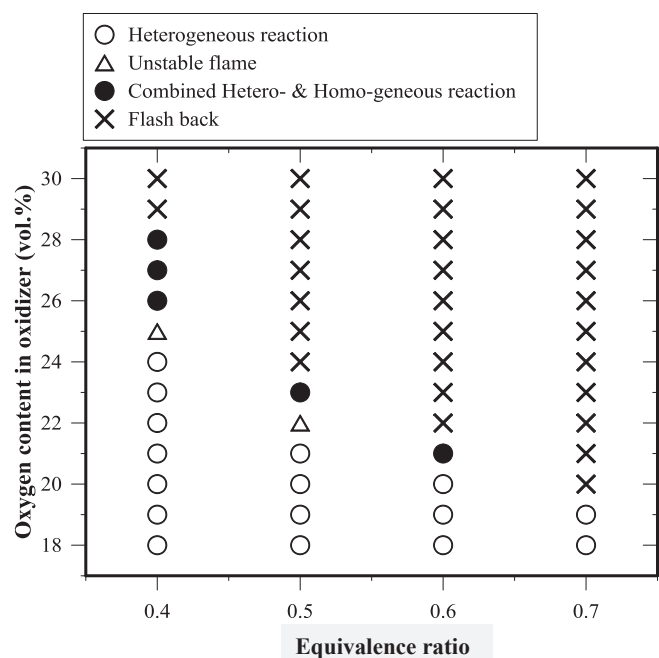


Fig. 9. The operating range of TP reactor for various equivalence ratios and oxygen contents in the oxidizer in the condition of fixed flow velocity equal to 5 m/s.

the essential factors to sustain catalytic oxy-fuel reaction in the TP reactor.

3.2. RCC (Replaceable catalyst-channel) reactor

In the above experiments of TP reactor, the operational control of flame stabilization mechanism in a small-scale channel and operational manipulation of fuel competition between homogeneous and heterogeneous reactions over platinum are the two essential challenges to achieve high fuel conversion. In order to cope with aforementioned inhibitions, the configuration of catalyst segmentation with cavities in a channel is engaged in this section. Fig. 10 shows the hydrogen-air combustion behaviors of the RCC reactor with five different channel configurations in the conditions of equivalence ratio equal to 0.6 and flow velocity equal to 10 m/s. The exposure time of the photographs is fixed at 1/25 s. There is no chemical reaction in the non-catalytic straight channel in Fig. 10(a), but a homogeneous reaction in a cavity channel, as shown in Fig. 10(b). It appears that the presence of cavities in a channel provides a low-velocity asylum to stabilize premixed hydrogen flame. For the three catalyst channels, single catalyst, segmented catalyst as well as segmented catalyst with cavities, respectively, catalytically supported combustion occurs for all the cases in the RCC reactor. In the single catalyst channel, as shown in Fig. 10(c), catalytically supported combustion is seen to anchor on the catalyst surface, such that the competition for fuel and radicals between homogeneous and heterogeneous reaction is anticipated. In the segmented catalytic channels without and with cavities, as shown in Fig. 10(d) and (e), the catalytically stabilized combustion can be sustained in either inert walls or cavities between two neighboring segment catalysts. The upstream heterogeneous reaction is regarded to provide radicals and catalytically-induced exothermicity for assisting the ensuing homogeneous ignition/combustion instead of competing for fuel and radicals. The detailed explanation for hydrogen catalytic combustion in the segmented catalyst and cavity channels is also addressed in our previous papers [25–27].

Fig. 11 demonstrates the oxy-fuel combustion of five different channels configurations in the conditions of equivalence ratio equal to 0.6 and flow velocity equal to 10 m/s as well as minimum oxygen contents in the oxidizer for sustaining homogeneous reaction. For a straight channel without catalyst surface, the minimum oxygen content required for maintaining homogeneous reaction in a channel is 28% in the oxidizer. Excessive oxygen is necessitated to increase flame temperature for overcoming the thermal quenching induced by carbon dioxide. For the cavity channel case, the existence of cavity in the channel not only provides a flame stabilization mechanism for oxy-fuel combustion, but also significantly reduces the oxygen content to 25% in the oxidizer to initiate oxy-combustion. The function of the cavity in the channel enables to provide a low-speed recirculation zone for flow field and thermal energy storage for flame stabilization, so as to reduce the minimum demand of oxygen content in the oxidizer. However, in the case of the single catalyst channel, the minimum oxygen content can be reduced to 26% to sustain catalytically stabilized homogenous reaction compared with the non-catalytic straight channel. The minimum oxygen content could further be reduced to 25% in segmented catalytic channel and 23% in segmented catalytic channel with cavities. Segmented catalyst overcomes the challenge of oxy-fuel environment caused by high heat capacity of CO_2 and initiates the heterogeneous reaction. Heterogeneous reaction yields catalytically-induced exothermicity and abundant intermediate species. The catalytically induced exothermicity would be absorbed by carbon dioxide and catalyst surface. Carbon dioxide also absorbs and emits thermal radiation. The mixture is expected to preheating via radiative heat transfer from illuminating catalyst surface and carbon dioxide. In addition, the convective heat transfer in oxy-fuel combustion cannot be neglected. The convective heat transfer coefficient is influenced by the flow velocity and gas properties such as viscosity, thermal conductivity, heat capacity and density. Owing to slightly higher thermal conductivity of CO_2 than N_2 , as seen in Table 1, there is no significant difference on conductive heat transfer when compared with air-combustion. For convective heat transfer at identical velocity, however, CO_2 has lower kinematic viscosity and leads to a

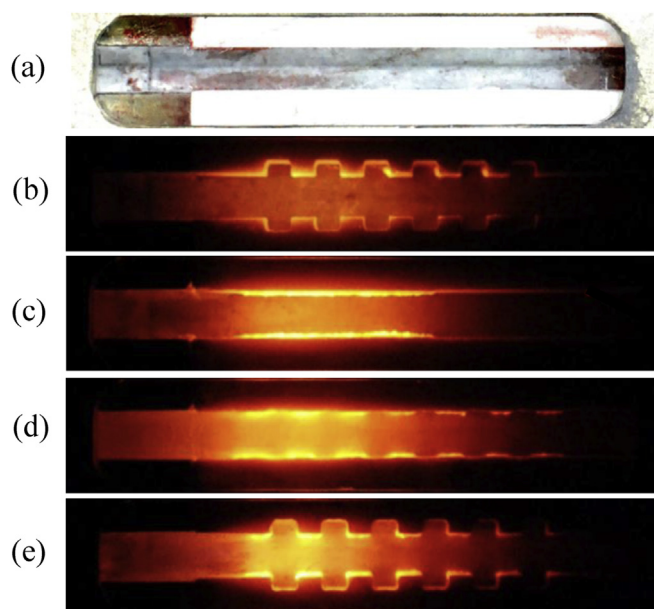


Fig. 10. The hydrogen-air combustion behaviors of RCC reactor with five different channel configurations in the condition of equivalence ratio equal to 0.6 and flow velocity equal to 10 m/s. (a) Straight channel, (b) cavity channel, (c) single catalytic channel, (d) segmented catalytic channel, (e) segmented catalytic channel with cavities.

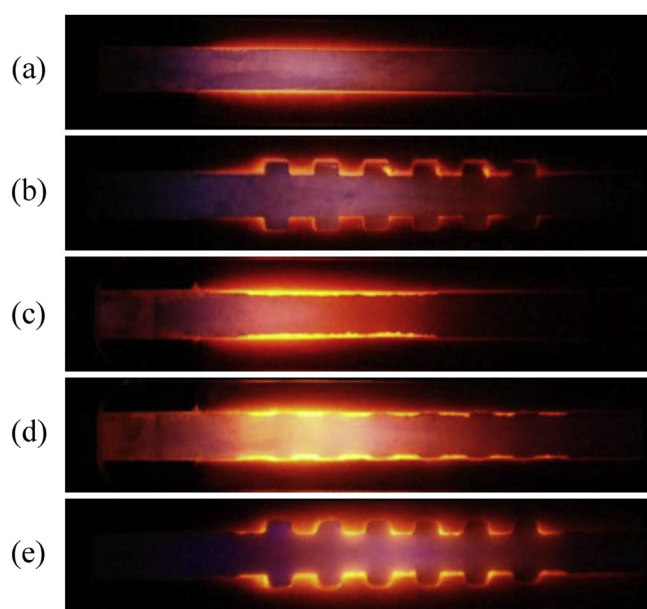


Fig. 11. The oxy-fuel combustion of five different channels configurations in the condition of equivalence ratio equal to 0.6 and flow velocity equal to 10 m/s as well as minimum oxygen contents in the oxidizer for sustaining homogeneous reaction. (a) Straight channel, (b) cavity channel, (c) single catalytic channel, (d) segmented catalytic channel, (e) segmented catalytic channel with cavities.

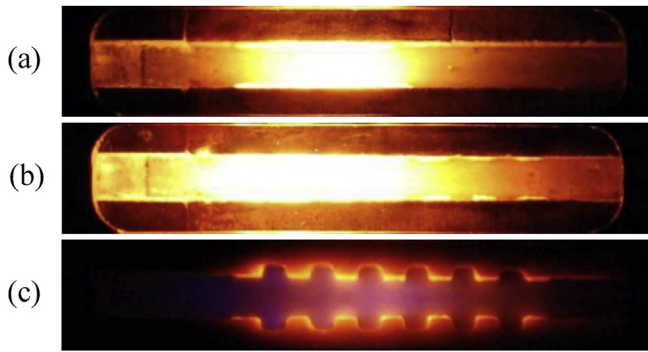


Fig. 12. The chemical reactions in single catalytic channel, and segmented catalytic channels without and with cavities in the condition of equivalence ratio equal to 0.6 and flow velocity equal to 10 m/s and fixed oxygen content equal to 23% in the oxidizer.

larger Reynolds number, and thus a higher convective heat transfer coefficient. Consequently, the effect of radiative and convective heat transfer becomes more significant in oxy-fuel combustion that enhances preheating of the mixture gas in the channel. By inheriting radicals from neighboring heterogeneous reaction and preheating via aforementioned thermal effect, homogeneous reaction can be induced and stabilized in inert place and cavity between two neighboring segment catalysts. Especially, the existence of cavity not only provides a low-velocity region for flame stabilization, but also supplies thermal energy to heat up the adjacent catalyst segment and to enhance catalytic combustion. The configuration of catalyst segmentation and cavity in a channel is confirmed to diminish the demand of oxygen content in the oxidizer and facilitate the inception of catalytic oxy-fuel combustion.

It is of interest to note that the color of homogeneous reaction in oxy-fuel condition is white with light blue, unlike orange color in air-fuel condition. It is believed that the carbon monoxide yields in the oxy-fuel reaction and possibly from the reaction of $\text{CO}_2 + \text{H} = \text{CO} + \text{OH}$. This situation is also discovered in oxy-fuel combustion experiments. Fig. 12 shows the chemical reactions in the single catalytic channel, and segmented catalyst channels without and with cavities in the condition of equivalence ratio equal to 0.6 and flow velocity equal to 10 m/s and fixed oxygen content of 23% in the oxidizer. Table 2 shows the corresponding flue gas emissions analyzed by GC (gas chromatography). The experimental results exhibit that only heterogeneous reaction presented in both cases of single and segmented catalyst channel without cavities, whereas homogeneous and heterogeneous reactions coexisted in the case of segmented catalyst channel with cavities. The analysis of flue gas components contains little carbon monoxide and large amount of the remaining hydrogen in both cases of single and segmented catalytic channel without cavities. Hydrogen conversion ratios are 47.4% for single catalyst channel and 50.7% for segmented catalyst channel without cavities. Once homogeneous reaction is initiated in the segmented catalytic channel with cavities, carbon monoxide content in flue gas soars to 0.54% and complete hydrogen conversion is reached. It is noted that carbon monoxide exists in three catalytic cases for pure heterogeneous reaction and coexistence of homogeneous and heterogeneous reaction. It is believed that the heterogeneous reaction heats up the ambient CO_2 in the vicinity of the catalytic surface and localized CO_2 close to the catalyst surface reacts with H radical provided by heterogeneous reaction and generate CO and OH reaction. On the contrary, it is a small probability in CO_2 adsorbed on the catalyst surface and reacting with H to produce the resulting CO and OH due to low stick coefficient of CO_2 . Furthermore, sticking coefficient of CO is large than that of H_2 , but less than O_2 . Some catalytically induced CO can be adsorbed on the

Table 2

The measured gas components of flue gas in three catalyst layouts of micro-channel.

The channel of catalyst layouts	CO concentration (vol.%)	H_2 concentration (vol.%)	H_2 conversion rate (%)
Single catalyst	0.02	13.23	47.4
Segmented catalyst	0.02	12.41	50.7
Segmented catalyst with cavities	0.54	0.02	99.94

active site of catalyst surface to retard hydrogen heterogeneous reaction over the channel. The remaining CO may diffuse to the flue gas. The small amount of CO in the single and segmented catalyst channels is detected due to localized CO_2 decomposition reaction and CO adsorption by catalyst. However, CO production is primarily from homogeneous reaction which provides high temperature and abundant H radicals. High temperature on catalyst surface leads to enhanced CO desorption than CO adsorption over the catalyst surface. Besides, hydrogen has inherently large thermal diffusivity compared to carbon monoxide, so that the heterogeneous reaction of H_2 is more active than that of CO in the channel. It explains that segmented catalytic channel with cavities has high hydrogen conversion ratio with high CO content in flue gas.

In order to investigate the effect of the flow velocity on the segmented catalytic channel with cavities, five different flow conditions of oxy-hydrogen reaction at fixed conditions of 0.6 equivalence ratio and 23% oxygen content are addressed. When flow velocities range from 5 m/s to 10 m/s, catalytically-induced homogeneous reaction can be sustained in the cavities and the flame anchoring position would move downstream depending upon increasing flow velocities. Once the flow velocity reaches 12.5 m/s, homogeneous reaction cannot be sustained in the channel, but heterogeneous reaction exists in the channel. However, the illumination of channel surface in Fig. 13(d) and (e) is higher than these in

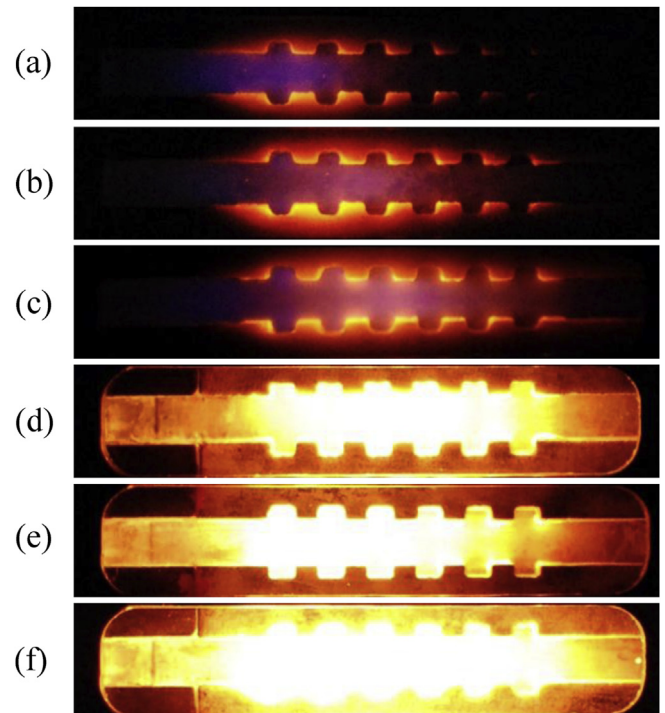


Fig. 13. The oxy-fuel reaction of segmented catalytic channel with cavities in various flow velocities, (a) 5 m/s, (b) 7.5 m/s, (c) 10 m/s, (d) 12.5 m/s and (e) 15 m/s and (f) 17.5 m/s, respectively.

Fig. 13(a), (b) and 13(c). It is because increasing the flow velocity simultaneously increases the total hydrogen content in the mixture, so as to enhance the heterogeneous reaction over the catalytic surface without the fuel competition by homogeneous reaction.

The segmented catalyst and cavities presented in the channel can apparently extend flammability limit, improve combustion stability, and reduce oxygen content in the oxidizer. Catalytically stabilized oxy-fuel combustion can accomplish high fuel conversion, but accompanied with plentiful CO production. The mechanism of CO production in catalytic combustion is not completely clear, but it is anticipated that the CO_2 decomposition through the reaction of $\text{CO}_2 + \text{H} = \text{CO} + \text{OH}$ (homogeneous reaction) is facilitated by offering chemical radicals and thermal energy in the vicinity of catalyst surface. As to CO_2 decomposition through $2\text{CO}_2^* = 2\text{CO}^* + \text{O}_2$ on the catalyst surface (heterogeneous reaction), it has to be further identified.

4. Conclusions

There are two kinds of small-scale reactors, tubular reactor and channel reactor, respectively, used in this study for examining the effect of CO_2 dilution on oxy-fuel reaction over catalytic surface. In the tubular reactor, stainless steel tube and platinum tube are used to clarify the effect of catalyst on oxy-fuel reaction. The results show that the minimal oxygen content requested for sustaining oxy-fuel reaction in a tubular reactor can reduce to 21% in tubular platinum case. Besides, the interaction between heterogeneous and homogeneous reaction on tubular platinum reactor are elucidated according to the resulting surface temperatures of the tube and fuel conversion ratios. Carbon dioxide would absorb chemically-induced heat release of hydrogen, but in the meantime heat up the flowing mixture via radiative and convective heat transfer. But a lack of flame stabilization mechanism in a miniature tube and fuel competition between hetero- and homogeneous reaction are two primary challenges to extend flammability limit and reduce oxygen content in the oxidizer.

In the channel reactor five different layouts are performed and compared in air-fuel and oxy-fuel environments. The results demonstrate that the segmented catalyst with cavities has minimal oxygen concentration to hold catalytically stabilized thermal flame in a channel, and performs approximately complete fuel conversion. Beside, CO content in flue gas in the case of segmented catalyst with cavities is certainly higher than that of single catalyst and segmented catalyst cases. The decomposition of CO_2 is induced in the vicinity of the catalytic surface due to providing radicals and requested thermal energy. The effect of CO_2 on catalyst in oxy-fuel environment would influence in terms of heat transfer, chemical reactivity as well as interplay between hetero- and homogeneous reaction.

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