

The Role of Hydrogen Pre-reaction for Methane Catalytic Ignition

Hsu, Hung-Wei¹, Chen, Jyh-Yuan² and Chao, Yei-Chin¹

¹Department of Aeronautics and Astronautics
National Cheng Kung University
Tainan, Taiwan, 701, R.O.C.
ycchao@mail.ncku.edu.tw

²Department of Mechanical Engineering
University of California
Berkeley, CA, 94720-1740, U.S.A.
jychen@newton.me.berkeley.edu

Introduction

Catalytic combustion is known to provide an attractive way to enhance the combustion stability while decreasing pollutant emission. Catalytic combustion has been used to stabilize lean combustion without significant pressure loss and has a wide operation range for various fuels. However difficulties in the light-off process of catalyst have significantly hampered practical applications. This becomes the most important issue for the developments of catalytic combustion, especially in gaseous hydrocarbon and gasified biomass fuels. From the viewpoint of ignition ability, addition of hydrogen to the initial mixture may help reduce the ignition temperature, because ignition of hydrogen on platinum can occur at room temperature. The thermal effect is intuitively thought to be the main factor of the hydrogen-assisted catalytic ignition process [1, 2], but evidence of this inference is lacking. The inference of the thermal effect results in methane ignition and reaction on the catalyst surface may be questionable for hydrogen due to its high diffusivity and sticking coefficient. In addition, hydroxyl radicals are the major intermediate of H₂ reaction when hydrogen is pre-fed to assist the methane ignition [3, 4]. The effects of hydrogen on radical pools on the surface need to be explored. To this end, experimental measurements of transient behaviors of hydrogen-assisted methane-air catalytic combustion are conducted. Two-dimensional numerical simulations with a multi-step gas phase mechanism and surface reaction mechanism are also performed to provide a better understanding of the underlined processes.

Experimental and Numerical System

The experimental apparatus consists of a lab-type catalytic combustion device, air/fuel supply and control system, fuel mixer, and measurement systems. Air and fuels are supplied from a compressor and gas cylinders respectively, and they are metered by mass flow controllers. Fuel and air flow through a static mixer to reach a desired mixture concentration. The mixture temperatures are measured by thermocouples placed at the catalyst outlet. Emissions at the catalyst exit are analyzed by the gas analyzer system. Time dependent two-dimensional numerical model is developed with multi-steps gaseous and surface reactions mechanism. The surface chemistry model uses a multi-step mechanism of methane surface mechanism developed by Deutschmann et al. [1].

Results and Discussions

Experiments with three ways of feeding the catalyst are conducted to explore the effect of hydrogen on subsequent ignition of H₂/CH₄/air mixtures. In method one, the catalyst is fed with a hydrogen-air mixture first and then followed by the H₂/CH₄/air mixture. This method is

referred to as the 'H₂ pre-reaction'. The second method feeds the catalyst directly with the H₂/CH₄/air mixture. In method three, the catalyst is fed with a CH₄/air mixture first and followed by the H₂/CH₄/air mixture. If the role of hydrogen is merely to provide heat for subsequent ignition, the CH₄ conversion is expected the same for these three cases as the same the H₂/CH₄/air mixture is fed after the catalyst is heated up. Figure 1 shows the CH₄ conversions of the three cases with the CH₄ volume concentration fixed at 3.5%. The conversions of CH₄ reveal three regimes characterized by H₂ concentration. When the volume concentration of H₂ is lower than 2.5%, only a small amount of CH₄ is converted into products on the catalyst surface for all cases. Methane did not get ignited when H₂ content is low. Catalytic ignition of methane always occurs when the subsequent H₂ feed volume concentration reaches 3%. If the volume concentration of H₂ is 2.5%, methane can be ignited successfully for both the direct feeding and the H₂ pre-reaction, but not for the third method with CH₄/air feeding first. The conversions of CH₄ for direct feeding and CH₄ feeding first are lower than hydrogen-assisted. This implies that the use of H₂ pre-reacting plays an important role in the subsequent CH₄ catalytic combustion and dominates the overall reaction process. It is believed that H₂ pre-reaction not only facilitates a hot surface but also promotes high levels of radical species and bare active sites for the subsequent fuel mixture.

Numerical simulation is used to delineate the various factors influencing the light-off of CH₄ in the presence of H₂. For the case without H₂ pre-reaction, the surface temperature is set to that resulted by the H₂ pre-reaction. Important factors can be discovered by monitoring the time evolutions of surface species. For the case with lean H₂ (H₂=2.5% and CH₄=4% at 1.45 m/s), the surface C(*) and O(*) coverage on the catalyst at 0.1 sec are shown in Figure 2(a) for combustible mixture flowing directly over a hot platinum channel and for the hydrogen-assisted case. The numerical results show that the active sites near the front end of catalyst are occupied by C(*) for the direct feeding case. This phenomenon is not found for hydrogen-assisted catalytic ignition during the same time period under the same operation condition. In the direct feeding case, the downstream section of catalyst channel exhibits high O(*) coverage and low C(*). The above comparison reveals the plausible reason why the catalytic reaction can be ignited rapidly by H₂ pre-reaction, but slowly for the direct feeding case. However, if the concentration of H₂ increases beyond 3.5%, the surface coverage of C(*) becomes small (shown in Figure 2(b)) compared to the lean H₂ case. A successful ignition always occurs when the H₂ concentration is high. This is due to the high diffusivity of H₂ and the low activation energy of H₂ catalytic reaction. As is well known, H₂ catalytic reaction can be ignited at room temperature. Consequently, the heat release will promote the subsequent CH₄ ignition if the temperature is sufficiently high. Similarly, the CH₄/H₂/air mixture can be ignited by the strong H₂ reaction that releases adequate energy to initiate CH₄ catalytic reaction. As such the surface coverage of C(*) is reduced when the concentration of H₂ is high. This implies that the inhibition of C(*) coverage by H₂ pre-reaction becomes a key factor when the H₂ content is low.

An analysis of the reaction paths in the CH₄ surface mechanism [1], reveals that C(*) is created by CH(*) dissociation and consumed by combination with O(*). The competition for O(*) by H(*) and C(*) is thought to play the key role in the catalytic ignition of CH₄ when H₂ is present in the fuel. Before oxidation, CH₄ is absorbed and dissociated into 1 part of C(*) and 4 parts of H(*) on the platinum surface. Similarly, the dissociation of H₂ results in 2 parts of H(*) on the platinum surface. In order to continue the reaction process, both C(*) and H(*) must combine with O(*) to produce CO(*) and OH(*), respectively. Because the activation

energy in forming OH(*) is lower than CO(*), the combination step of OH(*) is faster than CO(*). If H₂ is pre-reacted, OH(*) and other species are already present on the surface before CH₄ is introduced. The existing OH(*) resulted by H₂ pre-reaction can combine with H(*) directly to form H₂O(*) reducing the need of O(*) temporarily. Therefore H₂ pre-reaction tends to promote a high probability of CO(*) combination and enhances the CH₄/H₂/air catalytic ignition due to the more energy released from CH₄ oxidation. If the heat release is high enough, a successful ignition will be ensured. This conjecture is investigated by numerical simulations. To create an imbalance in the competition, the rate constant of CH₄ adsorption is increased gradually for a series of runs with the CH₄/H₂/air mixture flowing over a hot platinum honeycomb channel (no H₂ is pre-reacted). The results are presented in Figure 3 showing that the C(*) coverage increases with CH₄ adsorption reaction rate. When the pre-exponential factor increases to 7.5×10^{18} , a large portion of active sites is covered by C(*), in excess of half the catalyst channel. Consequently, the O(*) coverage decreases with the increase of C(*). This means that C(*) can not combine with O(*) because more C(*) are formed from stronger CH₄ adsorption and the active sites are poisoned by C(*). Although the OH(*) effect may require further investigation, the critical role of H₂ pre-reaction in the inhibition of high C(*) coverage and in the subsequent enhancement of catalytic ignition of CH₄ is clearly demonstrated.

Conclusion

The role of H₂ pre-reaction for hydrogen-assisted methane catalytic ignition is examined in this study. Thermal effect is found not to be the only factor in the H₂/CH₄/air catalytic ignition assisted by H₂ pre-reaction. The key factors of H₂/CH₄/air mixture catalytic ignition can be classified by two parts: 1) Thermal effect: When the surface temperature is high enough, which can be achieved by H₂ reaction at a high level. In other words, if the combustible mixture contains a high level of H₂ or the catalyst surface temperature is sufficiently high, thermal effect dominates the catalytic ignition. 2) The H₂ pre-reaction can reduce the competition between C(*) and H(*) to combine with O(*). This is believed to be the key factor in hydrogen-assisted catalytic ignition of methane if the H₂ content is low or the temperature is low.

Reference

1. Deutschmann, O., Maier, L. I., Riedel, U., Stroemman, A. H., and Dibble, R. W., 2000, "Hydrogen Assisted Catalytic Combustion of Methane on Platinum," *Catalysis Today*, Vol. 59, pp. 141-150.
2. Tischer, S., Correa, C., and Deutschmann, O., 2001, "Transient three-dimensional simulation of a catalytic combustion monolith using detailed models for heterogeneous and homogeneous reactions and transport phenomena," *Catalysis Today*, Vol. 69 pp. 57-62
3. Dogwiler, U., Benz, P., and Mantzaras, J., 1999, "Two-dimensional modelling for catalytically stabilized combustion of a lean methane-air mixture with elementary homogeneous and heterogeneous chemical reactions," *Combustion and Flame*, Vol. 116 pp. 243-258.
4. Griffin, T. A., Pfefferle, L. D., Dyer, M. J., and Crosley, D. R., 1989, "The ignition of methane/ethane boundary layer flows by heated catalytic surfaces," *Combustion Science and Technology*, Vol. 65 pp. 19-37.

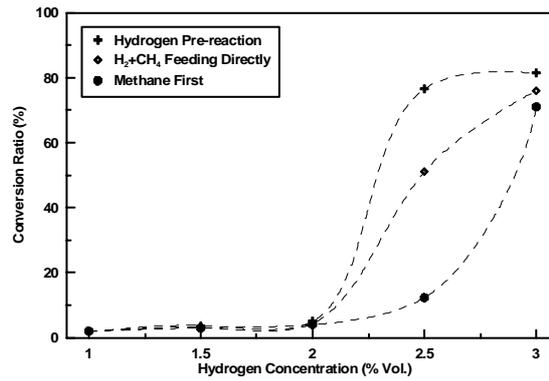


Figure 1 Methane conversions of H₂/CH₄/air for three ways of feedings: H₂ pre-reaction, direct feeding, and methane/air mixtures feeding first at ambient temperature. methane volume concentration is specified as 3.5%.

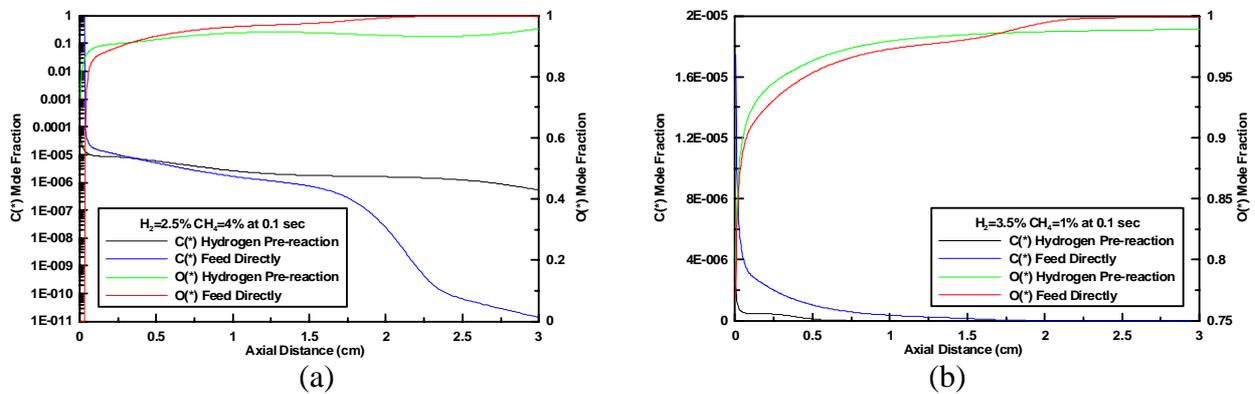


Figure 2 The coverage of C(*) and O(*) for hydrogen pre-reaction and feeding directly case at 0.1 sec. (a) H₂=2.5%, CH₄=4% (b) H₂=3.5%, CH₄=1%.

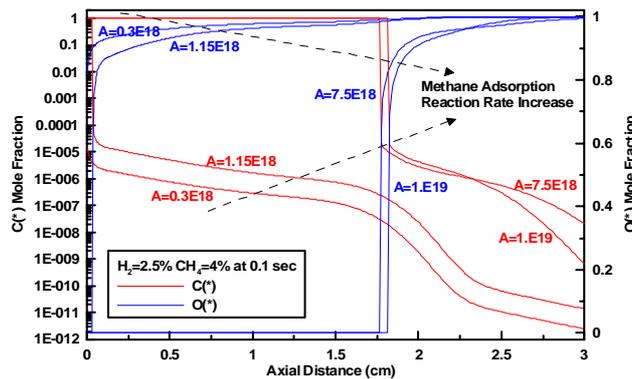


Figure 3 The coverage of C(*) and O(*) along the catalyst channel with various methane adsorption reaction rate (change pre-exponential factor).